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Abstract: Oceans constitute one of the most important reservoirs for mercury. In order to provide a first insight into the concentrations of Hg species in the Atlantic sector of the Southern Ocean a sampling campaign was carried out south of the Polar Front.
Water samples taken at discrete depths from the surface down to 300 m at five stations were analysed for total Hg (HgT), methylmercury (MeHg) and other interpretative parameters such as salinity, temperature, dissolved and particulate organic carbon, dissolved oxygen, chlorophyll and inorganic nutrients.
Results showed a high spatial variability in the concentrations of HgT and MeHg. HgT (0.93±0.69 ng L-1) and MeHg (0.26±0.12 ng L-1) levels were similar or higher than those reported in previous works in high latitude studies. The highest values were found at a location (-53°, 10°E) south of the South Polar Front, an area of strong gradients caused by the mixing of different water masses. Vertical profiles showed a great variability even for those stations sampled at the same location or an area dominated by the same oceanographic features. A decrease of HgT and a consequent increase in MeHg with depth was observed in some sites, suggesting the occurrence of Hg-methylation process, while at other stations, a concurrent decrease or increase of both mercury species was observed. In spite of these differences, an overall positive correlation between HgT and MeHg was observed. Differences between vertical profiles of Hg species were attributed to favourable environmental conditions for Hg methylation. The highest proportion of MeHg (% of HgT) was observed in sites with low dissolved oxygen or highest estimated remineralization rates.
The results obtained in this study show that the Hg distribution and speciation in the Atlantic sector of the SO is comparable (or in some sites higher) to the ones published for the other open ocean regions. However, the concentrations of MeHg in this area are more dependent on the environmental conditions than on the total concentration of Hg present in the water.

Lisbon on June 21th, 2016

Dear Editor

Thank you for sending us the reviewer's comments of the manuscript entitled "Mercury and methylmercury in the Atlantic sector of the Southern Ocean" by Canário et al submitted to the special issue of Deep Sea Research II.

We found all these remarks very useful and most interesting. All suggestions and comments were taken into consideration.

Please, do find enclosed the answers to the reviewers and the revised version of the manuscript.

With my best regards

Best Regards

João Canário

(Corresponding author)

Comments and modifications made on the first version of the manuscript "*Mercury and methylmercury in the Atlantic sector of the Southern Ocean*"– by Canário et al.

Comments

Editor

Enclosed are the reviews of your paper, one of them is somewhat favorable, while another contains serious criticism. In particular, one of the referees indicated issues of contamination and expressed concerns about very high values measured in your study. This prompted this reviewer to reject paper. Since the other referee only requested "minor revision", I would like to give you the opportunity to reply on the comments of both referees, provide very clear description of your methodology and attempt to rectify issue of obtained high values.

Dear editor. Thank you for sending us the comments from both reviewers. All of them were analysed in detail and let us made a profound revision of the first version of the manuscript.
The big issue of this manuscript was the relatively highest levels obtained that suggested contamination. This was the main point of reviewer 2 that assumed a contamination issue based on the concentration of acid used in the preservation of the samples. However, if this was true, we would get the same problem with the blanks and with the obtained concentrations using the certified reference materials, and this was not the case. As we explained in the comments to the reviewer 2 only some contamination was detected in two lab blanks and we believe that was due to a decontamination issue during the material cleaning process. Thus, we are pretty confident about our data.
As reviewer 2 suggested, we sent him an email answering his concerns but so far we did not get any response.
We believe that the revised version of the manuscript is more clear and the gaps identified by both referees are now settled.

Reviewer 1

a) *Hg data, especially MeHg, in field studies are very rare and potentially very valuable for understanding the global biogeochemical cycling of this element. It is particularly unusual to have field MeHg data for remote waters of the Southern Ocean, where physical conditions are demanding and complex water movements are the norm. While the data generated here for dissolved mercury species are nice to have, this paper would have been better had the authors also measured particulate mercury species, and had they measured Hg0. With these additional measurements, fewer speculations would have been necessary.*

We thank the positive feedback from this reviewer and acknowledge the comment about the measurements of particulate and elemental mercury. These measurements would provide more information about the Hg cycle in this part of the Atlantic Ocean however, this was not possible during this campaign. We believe that in the next opportunity the quantification of this mercury species will be a key point.

b) *A much more complete description of the "clean" sampling techniques would be appropriate. Referring to iron papers may not be entirely appropriate.*

The materials and methods section had a profound revision not only based on this comment but also based on the comments provided by the reviewer 2. We believe that in the revised version of the manuscript this issue is now more accurate.

c) *On page 11, paragraph of "Mercury and methylmercury", the data reported in the text were not consistent with the data in Table.1 (e.g. HgT and MeHg ranges).*

The reviewer comment is correct. We made revision in this section and not only corrected the errors but also reformulate the entire section.

d) *For Table.2, there are more HgT and MeHg data published in recent years (e.g. GEOTRACES cruises, Bowman et al., 2015; Hammerschmidt and Bowman, 2012)*

The information concerning this papers as well as from another paper recently published (Bratkic et al 2016) was included on the table as well as on the discussion section. A new table 2, compiling all these new data, is now included in the new version of the manuscript.

e) *On page 13, Compared to other studies, HgT concentrations at stations 84, 91 and 143 were apparently higher. The authors suggested this could be attributed to local sources, such as large scale Hg deposition. If this is the case, why are concentrations at station 140 (which is close to station 91) not higher at the surface?*

In stations 91 and 140 the sampling occurred during the phytoplankton bloom but at different stages. While in st. 9 sampling took place in the beginning of the bloom, in st. 140 sampling occurred in a later stage. This information is presented in table 1. It is well known that dissolved Hg can be easily uptaked by phytoplankton (see as an example: Zhong and Whang, 2009, ES&T or Faucheur et al., 2014, Env. Tox and Chem.) so based on this published works it is expected that in st. 140 the levels of both dissolved Hg and MeHg would be lower (than in st. 91), that was what we found.
A similar behaviour among these stations (91 and 140) was observed during the same cruise in the case of dissolved iron (Laglera et al., 2013) as this element is known to be assimilated by phytoplankton species during the development of the bloom. Based on this, we completed the discussion of this subject in the revised version of the manuscript.

f) On page 14, paragraph about fig. 7, levels of MeHg and MeHg/HgT ratios in waters are not just controlled by methylation processes, it should be a net result of methylation (mainly biotic) and demethylation (both photochemical and biotic) processes, as well as release of Hg and MeHg from remineralization. Also, mixing with lateral or deep waters may need to be taken into consideration. Also in the same paragraph the authors showed a regression equation, where if HgT is zero, MeHg would be 0.09 ng/L. That doesn't make any sense, since by definition HgT should be always > MeHg. A fuller discussion of these points is appropriate.

The referee is right about the amount of processes that could be involved in the MeHg-HgT equilibria, a sentence including these processes (remineralization and lateral or deep mixing) has been includedin the revised version of the manuscript.

Regarding the issue of the regression equation, our intention was not to infer values of MeHg from the values of HgT and using this equation. The aim of this figure was just to show a positive correlation (statistically significative) between both variables. However, the observation made by the referee is true and this fact is due to an artifact of the model. Thus, to get a MeHg 0 concentration when HgT is 0, the regression coefficient should be 1 and this is quite difficult when having such a great number of data. In order to avoid misinterpretation of the data, a new figure 7 has been plotted without including the regression equation.

In fig. 7, the authors asserted that two open circles (st. 84) were excluded due to the possible strong net methylation process. However, high MeHg found at depth 100-200 m at st. 84 did not necessarily indicate a strong net methylation. Especially the authors explained that UCDW intrusion brought low oxygen and then enhanced in-situ MeHg production at station 84. But what if it's just simply due to mixing (UCDW may directly bring in high MeHg?). Solid evidence is needed to legitimately exclude those points.

The reviewer is right about this issue. The fact to exclude some of the values was due to the unfiltered water samples from station 84. The explanation for this issue has two major points: (1) is the fact that these samples (as mentioned before) are unfiltered so the total MeHg concentrations measured reflect not only the dissolved fraction but also the particulate. In spite that the concentration of suspended matter is low, the absolute concentrations of this Hg specie in the particulate phase is higher due to their ad(ab)sortion capacity (biogenic or not). In other way (2) with or without particles and of course transport and mixing. Based on these issues we completely reformulated this section.

g) *Discussion at section 4.3 is really confusing. Page 17, about Table 3 (please explain the difference between positive and negative numbers.) First, the correlation matrix results showing a significant relationship may mean nothing but a coincidence. Second, the authors asserted that "POSITIVE" correlations were obtained between both dissolved HgT and MeHg with respect to temperature. However the values in the table were both negative, shouldn't these mean NEGATIVE correlations? There's one sentence in this paragraph that was not clear at all---"Warmer waters with higher organic substrate increase bacterial activity and as a result, the concentrations of HgT and MeHg in the water column."*

In table 3 positive number mean positive correlations (Table caption has been rewritten) while negative number indicate negative correlations. Both positive and negative correlations are with 95% confidence level. We are not pretty sure about what the referee mean coincidence because this statistical analysis is commonly used in data analysis for environmental studies (e.g. Geiß et al., 1996, Chemometrics and Intelligent Laboratory Systems).

Concerning the second and the third part of the comment, the referee is right about the correlation with temperature. In fact, the correlation is negative for both Hg and MeHg and so the increase of bacterial activity with the increase of temperature does not make any sense. The negative correlation of HgT and temperature suggests that in cooler waters the amount of dissolved HgT is higher and therefore it is expected that MeHg will be also higher, if we assume that this HgT is available for methylation. Since the biotic methylation process is expected to occur in warmer waters (higher microbial activity), our results suggests that the amount of Hg available for methylation is a key factor for having more or less MeHg in this systems and consequently not the bacterial activity.

According to the referee comment and the above explanation the section 4.3 was reformulated.

h) *While there is a lot of speculation pointing to microbial processes, did anyone actually measure the bacterial production or metabolism on this cruise?*

In this cruise no one measured bacterial production or metabolism. However, Iversen et al (this issue) measured respiration rates in fecal pelets produced by salpas (zooplankton). Results obtained by the authors showed that highest respiration rates were found in warm waters at the surface or subsurface and in stations closer to the equator. Thus we may assume that the same is true for bacteria metabolism but our option is not including this information in the manuscript since it is a extrapolation that may not be real.

i) *There appear to be some problems with the figures and tables. Please check through them all. Some problems I noticed are: Fig 3: wrong units for phosphate and silicate. Tables 1, 2: unit styles are not consistent (e.g. W m-2 and ng/L). For ranges, use dash (-).*

The referee is right about this issue. All corrections were made accordingly.

Reviewer 2

j) *I deeply regret that i cannot recommend the manuscript for publication. I have serious doubts about the quality and validity of the measurements. Both tHg and MeHg data is much higher than all other open ocean studies. Global tHg do not exceed 2pM (0.4ng/L), and mean concentrations are usually close to or below 1pM (0.2ng/L). MeHg is a fraction of tHG that usually does not exceed 60%. The authors present data that is on average 5x higher, reaching up to 18pM (3.6 ng/L) for tHg. Indeed we found slightly higher tHg values (1.35pM = 0.27 ng/L) for the Southern Ocean (Cossa, 2011), but our highest values (2pM = 0.4ng/L) where in proximity of the Antarctic continent. Likewise, our MeHg for the SO where at the high end (0.5pM = 0.1 ng/L) of the values, typically measured in the subsurface open ocean (0.25pM = 0.05ng/L), but this is nowhere close to what the present study shows for the surface open ocean (2.5pM = 0.5ng/L), where MeHg are usually much lower. A recently published paper by Bratic (GBC, 2016) presents tHg and MeHg in the South Atlantic along 40°S, very close to the present study, and finds also much lower values. I tried to follow the authors explications for this, but i come to the conclusion that there must be some contamination issue. One reason might be that the authors used 7.5 mL HCL per 40 mL seawater sample (almost 20% v:v). This is very unusual, as we typically acidify to 0.4%, and might be the very high blank contribution. I have also tried to use the PSA Merlin to measure tHg in seawater, but the detection limit is insufficient. The authors mention no modification to the equipment to overcome this issue. Given the facts i see no other option but to reject the manuscript in its present form. I am available, if the authors wish to contact me directly.*

We thank the reviewer for the comments to the manuscript. We also thank him for his availability to let us discuss this subjects directly which we truly appreciate.

We made a carefully reading to your comments and some of them make sense according to the information we provide in the manuscript particularly the ones related with the analytical methodologies, QA/QC and the relatively high concentrations obtained that, in some, cases, may suggest contamination issues.

Thus, our comments are:

i. Analytical methodologies

The analytical methodologies used in our paper are the ones currently used and published in the literature, namely by EPA, several papers from my lab and in several Canadian laboratories. The use of 7.5 mL HCl (Hg-free/before Br/BrO_3) for HgT were the methods previously used in Environment in Dr. Laurier Poissant laboratory. Actually, I believe this technique was implemented by Dr. Daniel Cossa, a previous researcher there. It was also in this government laboratory that the MeHg analysis in the samples were made. QA/QC were always taken into account by the use of spikes, replicates and CRM.

Additionally, for several samples the HgT concentrations were determined in both laboratories (PT and CAN) and the results were the same within the analytical error and by using different equipment (PSA in PT and Tekran there).

Concerning MeHg analysis the amount of HCl was not the 7.5 mL but the samples were acidified at 0.5% according to EPA 1630 and the Canadian laboratory protocols.

In conclusion we will have provided a more detailed description of the methodologies and the QA/QC control in the new version of the manuscript.

ii. Contamination

Contamination is always a problem particularly when analysing trace levels in sea water and with this type of fieldwork. Field blanks (n=12), reagents blanks (n=12), and laboratory blanks (n=8) were always used during the analytical procedure. With the exception of two laboratory blanks (HgT) the blanks fluorescence signals were always equal or below the detection limit, calculated as 3 times the standard deviation of the blank average. We had a particularly concern by doing the lab and reagents blanks using the same reagents that were used in the field.

One other important issue was the use of certified reference materials to access the accuracy of our results. For the analysis in Portugal the BCR 579 (Hg in sea water) was used while in Canada they used ORMS-5 (Hg in river water) diluted 10 times with Milli-Q water at 1% HNO_3 (Hg-free). In both laboratories the obtained and certified values were not statistically different (t-test, 95% confidence level).

For MeHg analysis since no CRM was available the use of spikes and the the standard addition method for the quantification of this mercury species was used.

iii. Results

As mentioned previously MeHg concentrations were obtained in Canada while the majority of the HgT levels were obtained in PT and for 50% of the samples the same quantification was made also in Canada. In both laboratories, HgT levels were comparable within the analytical error (t-test – 95% confidence level).

In fact, some of our values are higher or in the same order of magnitude that the ones reported in literature namely the papers cited in the manuscript and also the ones reported by Bratkic (GBC, 2016), Hammerschmidt (MC, 2012) or Bowman (DSRII, 2015) and with the %MeHg within the reported levels for world oceans (up to 37%). The referee also mentioned that in Bratkic (2016) the values obtained at 40ºS were lower than the ones obtained in our study claiming that the distance between their and our work is not so pronounced that would justify the higher concentrations in our study. However, even Bratkic mentioned in page 111 last paragraph that the levels obtained for MeHg were lower than they were expected and justify these lower concentrations to cruise-related longer storage of the samples that may have also contributed to the overall low MeHg levels.

One other key question is the protocol for analysing filtered or unfiltered water. In fact, in the literature many of the obtained levels are for filtered water. In our case, and with the exception of station 84, the concentrations we presented were filtered. Interestingly is in st. 84 were the HgT (unfiltered) where the concentrations were higher. We all know that the amount of suspended particulate matter is quite low but the concentrations of both Hg and MeHg can be considerable higher in the particulate form compared to the dissolved form. Thus, our results are for total Hg and MeHg in both dissolved and particulate form for station 84 and this may explain the higher concentrations.

One other interesting fact is that the below surface the HgT and MeHg levels we present are in the same order of magnitude of several published works for world oceans.

Some explanations for the obtained values are presented in the paper. It should be noticed that highest values were only obtained in three of stations (84, 91 and 143) and particularly in station 84, being the concentrations in the other stations comparable to other published works. These levels were attributed to low chlorophyll, upwelling of low oxygenated waters and recently extinguished bloom. This events can bring more Hg species into the more superficial waters associated to the dissolved phase and to particulates from both biogenic and non-biogenic particles.

Finally, we have to mention that the Atlantic sector of the Southern Ocean is an area of volcanic activity particularly near south America and near the sub-Antarctic islands archipelagos (e.g. see: Browning et al, 2014, Geophysical Research Letters or Smith et al., 1986, Marine Geology) being this activity well known as a Hg source. Actually, my group measured concentrations as higher as 30 ng/L near the South Shetland Archipelago much more south than this work confirming the volcanism as an important source of dissolved Hg species.

Mercury and methylmercury in the Atlantic sector of the Southern Ocean

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Abstract

Oceans constitute one of the most important reservoirs for mercury. In order to provide a first insight into the concentrations of Hg species in the Atlantic sector of the Southern Ocean a sampling campaign was carried out south of the Polar Front.

Water samples taken at discrete depths from the surface down to 300 m at six stations were analysed for total Hg (HgT), methylmercury (MeHg) and other interpretative parameters such as salinity, temperature, dissolved and particulate organic carbon, dissolved oxygen, chlorophyll and inorganic nutrients.

Results showed a high spatial variability in the concentrations of HgT and MeHg. HgT (0.93±0.69 ng L^{-1}) and MeHg (0.26±0.12 ng L^{-1}) levels were similar or higher than those reported in previous works in high latitude studies. The highest values were found at a location (-53º, 10ºE) south of the South Polar Front, an area of strong gradients caused by the mixing of different water masses. Vertical profiles showed a great variability even for those stations sampled at the same location or an area dominated by the same oceanographic features. A decrease of HgT and a consequent increase in MeHg with depth was observed in some sites, suggesting the occurrence of Hg-methylation process, while at other stations, a concurrent decrease or increase of both mercury species was observed. In spite of these differences, an overall positive correlation between HgT and MeHg was observed. Differences between vertical profiles of Hg species were attributed to favourable environmental conditions for Hg methylation. The highest proportion of MeHg (% of HgT) was observed in sites with low dissolved oxygen or highest estimated remineralization rates.

The results obtained in this study show that the Hg distribution and speciation in the Atlantic sector of the SO is comparable (or in some sites higher) to the ones published for the other open ocean regions. However, the concentrations of MeHg in this area are more dependent on the environmental conditions than on the total concentration of Hg present in the water.

Keywords: mercury, methylmercury, Atlantic sector, Southern Ocean, Eddy Pump cruise

1. Introduction

Mercury (Hg) is a globally distributed pollutant that cycles between air, water, sediment, soil and organisms (Moreno et al., 2005) and is considered by the United Nations Environmental Program (UNEP) as a pollutant of great concern. Its presence in the environment is increased due to anthropogenic sources, and can create fatal health issues. Although anthropogenic emissions of Hg have been reduced by half in the last decades (Pacyna et al., 2001), ongoing contamination is still a worldwide problem. The conversion of inorganic Hg into methylmercury (MeHg; CH_3-Hg^+), a strong neurotoxin, is a critical step in its fate and toxicity. Interest in MeHg as an environmental contaminant first arose in the 1960's with reports of alkylmercury poisoning of marine life and humans in Japan, and birds and marine life in Sweden (Kiyoura, 1964; Johnels and Westermark, 1969). The net MeHg concentrations result from the balance between methylation and demethylation processes, which are not completely understood (Mason and Benoit, 2003). The most important factors influencing biological methylation are the availability of inorganic mercury and the nature of the microbial community (Mauro et al, 1999; Ullrich et al., 2001) modulated by physical and chemical parameters such as temperature, pH, salinity, organic carbon, and redox potential (Gilmour and Henry, 1991; Barkay et al., 1997; Ullrich et al., 2001; Mason and Benoit, 2003). Despite the paucity of information concerning sources, in situ production, biogeochemistry and bioaccumulation of MeHg in marine organisms, sediments appear as potentially significant sources of MeHg to food webs in the coastal zone (Mason et al., 1999; Gill et al., 1999; Covelli et al,. 1999; Langer et al., 2001; Hammerschmidt et al., 2004) and to the open ocean via hydrological or biological transport.

The ocean plays a central role in global mercury biogeochemical cycling. Within the ocean, Hg cycles among elemental (Hg^0), inorganic (Hg^{2+}), MeHg, dimethylmercury (DMHg), and particle-bound (Hg_P) forms (Mason and Fitzgerald, 1993). Atmospheric wet and dry depositions supply Hg to the surface ocean. In the mixed layer, Hg(II) may be (photo)reduced to Hg^0 and then re-emitted to the atmosphere (Qureshi et al., 2009). Hg(II) can also be adsorbed onto suspended organic-rich particulate matter (Hg_P). Deeper ocean remineralization of sinking particulate matter converts Hg_P to

dissolved Hg(II), thus resupplying Hg to the dissolved pool at depth (Mason et al., 1995; Amyot et al., 1997; Rolfhus and Fitzgerald, 2001; Fitzgerald et al., 2007, Strode et al., 2010). The hypoxic (low-oxygen) zone in the subsurface ocean is hypothesized to be an area of optimum biological methylation/demethylation processes (Sunderland et al., 2009; Lehnherr et al., 2011).

Burial of Hg_P in marine sediments is the terminal sink for Hg (Lamborg et al., 2003). Vertical profiles in ocean waters generally contain the signatures of three different processes:

i. in the mixed layer, total mercury (HgT) concentrations can exhibit a maximum or minimum relative to subsurface waters depending on the relative roles of sources (atmospheric deposition and upwelling of Hg-rich waters) and sinks (air-sea gas exchange and scavenging onto particles) (e.g. Zhang et al., 2014);
ii. the thermocline/intermediate waters (between the bottom of the mixed layer down to 1000 m depth) often display a local maximum in HgT (Zhang et al., 2014). This maximum has been interpreted as a Hg release from remineralization of sinking particulate matter. This maximum can also be interpreted as an anthropogenic signal from high-deposition regions through isopycnal transport or adsorption onto sinking particulate matter (Mason et al., 1998; Mason and Sullivan, 1999; Fitzgerald et al., 2007; Strode et al., 2010).
iii. in the deep ocean (>1000 m), HgT concentrations are relatively constant and sometimes slightly increase with depth (e.g., Laurier et al., 2004; Lamborg et al., 2012).

Many studies have been published about the Hg cycling in the world oceans (see references above) although, and with the exception of the biological compartments, less attention has been given to the Southern Ocean (SO). The first paper aiming to better understand the “abiotic” mercury cycle in the Southern Ocean was published by Cossa et al. (2011). In a scientific cruise between Tasmania and Antarctica, Cossa et al. (2011) found that Hg_T concentrations in water samples were comparable to recent measurements made in other parts of the world's oceans, however the Hg species distribution suggested distinct features in the SO Hg cycle: a net atmospheric Hg

deposition on surface water near the ice edge, an Hg enrichment in brine during sea ice formation, and a net methylation of Hg.

The work presented here contributes to the scientific efforts to understand the Hg cycling in the SO. During a RV Polarstern cruise in the Atlantic sector of the SO, several water profiles down to 300 m were sampled and analysed for total Hg, MeHg and other interpretative parameters (e.g. salinity, temperature, dissolved and particulate organic carbon, etc). The aim of this work is therefore to provide a first insight into the concentrations of Hg species in this area and to understand the processes responsible for their distribution, partitioning and speciation.

2. Material and Methods

2.1. Sampling

Sampling was carried out as part of the RV Polarstern "Eddy-Pump - ANTXXVIII/3" cruise along a longitudinal transect in the Atlantic sector of the Southern Ocean around latitude 50° S between January and March 2012 (Fig. 1).

Four different areas were sampled for Hg from east to west (see Table 1 for a more detailed position): in the east station 84 was located south of the Southern Polar Front (SPF) at 10ºE, two stations were located in the central Atlantic sector (stations 91 and 140) between the SPF and the Antarctic Polar Front (APF) where a large open ocean diatom bloom was investigated (up to 2 μg chl-a L^{-1}), the third region was further to the west (stations 163 and 174) between the APF and SPF at the North end of the South Georgia basin. Finally, station 143 was located close to South Georgia in the SPF (receiving iron inputs from the vicinity of the island, data not published). Details of the addressing fronts, their locations and biogeochemical features are provided in this issue (Strass et al.; Hope et al.; Puigcorbé et al.). The first station (st. 84) was characterized by low plankton biomass (<0.5 μg chl-a L^{-1}) in the euphotic layer (caused by a bloom in its declining stage; Cheah et al., this issue) and the surge of high iron/low oxygen waters of the Upper Circumpolar Deep Water (UCDW) which effect can be tracked up to 150 m deep (Puigcorbé et al., this issue). The second and third areas presented different development stages of a phytoplankton bloom. The last

area, close to South Georgia, provides information on the influence of the "Island effect" on the levels and biogeochemical cycle of Hg in these waters.

Profiles of temperature, salinity and pressure were measured with a Seabird SBE 911plus CTD (conductivity-temperature-density; Strass et al., this issue). Samples for chlorophyll a, DOC, POC and macronutrients (nitrate+nitrite, phosphate, silicic acid) analyses were collected from Niskin bottles attached to the CTD.

Since solar radiation may change and reduce some forms of mercury, direct solar radiation data have been included in Table 1 for each station during the sampling time (LI-COR 192SA light sensor). Half of the stations (84, 143 and 163) were sampled at night, while the rest of the stations showed a radiation range between 34-795 W m^{-2}.

All material and equipment used for mercury (and MeHg) storage and analysis (PTFE-Nalgene) were previously acid decontaminated. Briefly all material was washed with ultrapure water (Milli-Q Elemental System – 18.2 MΩ cm), two times with a solution of HCl (Suprapur-Merck) 20% (v/v) and after, rinsed again with Milli-Q and submerged in a HNO_3 (Hg-free) solution at 30% (v/v) for a week. Finally, the material was washed several times with Milli-Q water. All sampling flasks were filled with a solution of 1% HNO_3 (Hg-free) solution until sampling.

Samples for Hg and MeHg analyses were collected from the upper 300 m of the water column by means of 8 metal-free GOFLO bottles attached to a Kevlar line. With the exception of station 84 (unfiltered samples) all other samples were immediately filtered online (0.2 µm) by means of filtration sterile capsules (Sartobran 300) and collected in PTFE bottles (Nalgene). Samples for the determination of dissolved iron were collected in LDPE bottles (VWR) from the same GOFLO bottles used to collect Hg samples.

2.2. Analysis

Macronutrients

Macronutrients (PO_4^{3-}, $Si(OH)_4$, NO^{3-} and NO^{2-}) were measured onboard using a Technicon TRAACS800 autoalyzer (SealAnalytical). Details about analytical

protocols can be found in (Hoppe et al., in press) and elsewhere (Grasshoff et al., 1999).

Chlorophyll *a*

Chlorophyll a (Chl a) determinations were carried out using a 10-AU fluorometer (Turner). A more detailed description of the pretreatment and analysis procedure can be found in (Hoppe et al.).

Dissolved organic carbon (DOC) and Particulate organic carbon (POC)

Samples (~60 mL) for DOC analysis were filtered through pre-combusted GF/F filters using an HCl-cleaned glass filtration unit. The procedure was repeated 3 times for each sample in order to rinse the vials and the filtration unit, keeping the last filtrate for analysis. The final filtrate was collected directly into HCl-rinsed plastic (HDPE) bottles and frozen (-20°C) for further analysis on land. DOC was determined by high temperature catalytic oxidation (TOC-VCPN analyzer, Shimadzu) (Skoog et al., 1997). For external calibration potassium hydrogen phthalate (KHP, Merck) was used. Aliquots of the methanol extracts (50 mL) from the SPE samples were evaporated under N_2 gas flow to complete dryness and subsequently redissolved in 6.5 mL ultrapure water for DOC analysis (SPE-DOC). All samples were acidified (0.1 M HCl suprapur, Merck) and purged with O_2 for 5 min. Performance of the instrument was recorded by daily analysis of in-lab KHPstandard solutions and reference samples (deep sea reference, DSR, Hansell research lab). Repeatability of the DSR was >95% (ns = 42) and average blank values (water from the ship's MilliQ system processed as the the field samples) was 1.0 µM (± 2 µM std).

Samples for particulate organic carbon (POC) were filtered onto pre-combusted (15h, 500 °C) glass fibre filters (GF/F, Whatman). Filters were stored at -20 °C and processed according to Lorrain et al. (2003). Analyses were performed using a CHNS-O elemental analyser (EuroEA3000, HEKAtech).

Total mercury and methylmercury

After water collection samples were preserved with 7.5 mL (per 40 mL sample) of 33% HCl (Merck, Hg-free) for total mercury determinations and at 0.5% HCl for methylmercury.

Total Hg was determined applying the EPA 1631B method (EPA, 2002), using a PSA Merlin system by CV-AFS. Briefly, 1mL of bromine monochloride (BrCl) was added to the sample followed by the addition of 100µL of hydroxylamine solution to reduce the excess of BrCl. Total mercury was then determined by Cold Vapour Atomic Fluorescence (CV-AFS) Spectroscopy in PSA Millenium Merlin equipment using $SnCl_2$ as a reducing agent. Hg quantification was made using a calibration curve obtained by measuring several standards (0-30 ngL^{-1}) prepared by an adequate dilution of a 1000 ppm Merck standard solution.

Methylmercury concentrations were determined by GC-CV-AFS using automatic MERX equipment manufactured by Brooks Rand Labs, by distillation, aqueous phase ethylation buffered to pH 4.9 with an acetate buffer, purge and trap and separation by Gas Chromatography. Finally, Hg species were reduced to Hg^0 and detected by AFS. Concentrations were determined using the standard addition method. A stock standard solution of MeHg was prepared from the solid (MeHgCl – Aldrich) by dissolving the exact amount of compound in ethanol. This stock solution was used to spike the water samples before the extractions following the methodology described in Canário et al., (2006).

QA/QC control for mercury measurements

Analytical quality control was performed with calibrations and blanks on a daily basis and sample replicates.

Field blanks (n=12), reagents blanks (n=12), and laboratory blanks (n=8) were always used during the all analytical procedure. With the exception of two laboratory blanks (HgT) the blanks fluorescence signals were always equal or below the detection limit, calculated as 3 times the standard deviation of the blank average. We had a particularly concern by doing all blanks using the same reagents that were used in the field.

Certified reference materials were used tto access the accuracy of our results. Thus, BCR 579 (European Commission - Hg in sea water - certified: 1.9±0.5 ng L^{-1}; obtained: 1.6±0.3 ng L^{-1}, n=14) and ORMS-5 (NRCC Canada - Hg in river water - certified: 26.2±1.3 ng L^{-1}; obtained: 25.7±0.8 ng L^{-1}, n=14) diluted 10 times with Milli-Q water at 1% HNO_3 (Hg-free) were analysed for this purpose. The obtained

and certified values were not statistically different (t-test, 95% confidence level) (Miller and Miller, 2010).

Analytical recoveries of both Hg and MeHg were determined using the spike technique as ranged from 90 to 109 % for Hg and for MeHg from 92 to 103 %. Replicate samples were also used to assess variability of the data. The limits of detection (LOD) were calculated as three times the standard deviation from blanks repeated in every 20 samples to evaluate cross contamination and if the equipment were operating at the same conditions: for dissolved fraction Hg 0.10±0.015 ng L^{-1} and MeHg 0.02±0.0002 ng L^{-1}; repeatability was less than 6.0 % (n = 8), expressed as a percentage relative standard deviation (Miller and Miller, 2010).

3. Results

3.1 Salinity, temperature and dissolved oxygen

The vertical profiles of salinity (psu), temperature (ºC) and dissolved oxygen (µmol kg^{-1}) obtained for all the sites are presented in Fig. 2.

Salinity values ranged between 33.67-34.67 with lower values in the surface mixed layer (ML) (Table 1) and increased with depth at all the stations. Station 84, located south of the SPF, showed the highest salinity below the mixed layer, followed by the station 143. In the case of the mixed layer, salinity was also highest at station 84.

All stations showed a subsurface temperature minimum with temperatures below 2°C, indicative of Antarctic Winter Water, and that all were located south of the APF. The lowest values were found at station 84, followed by stations 143, 140 and 91 (in this order) with the highest temperatures at stations 163 and 174 (between 5 and 6°C). Below 200 meters, temperature values were similar among stations and close to 2°C.

The highest dissolved oxygen concentrations in the first 100 meters were found at station 84 followed by stations 91, 140 and 143 with the lowest dissolved oxygen levels found at stations 163 and 174. Below 100 m depth the trend changed with lowest oxygen concentrations at station 84 followed by station 143 and 140 and highest values at stations 91, 163 and 174.

In summary, the effect of the surging UCDW waters gave station 84 quite different properties from the rest of the stations, i.e.: lower temperature in the ML and higher

salinity and lower dissolved oxygen concentrations below the ML compared to the rest of the stations.

3.2 Nutrients

Nutrients vertical profiles for all sampling stations are presented in Figure 3. The highest values for all nutrients in surface waters (nitrite, nitrate, phosphate and silicate) were found at station 84 followed by stations 91 and 140 with the lowest values at stations 163 and 174. Silicate values in the ML were high at station 84, while at all other stations silicate has been depleted or brought close to limiting concentrations for diatom growth. Nutrient levels showed similar values at depth with the exception of silicate that remained higher at st. 84 as compared to the other stations caused by the surging of deep waters.

3.3 Chlorophyll *a*

The vertical profiles of chlorophyll (μg L^{-1}) in all sites are presented in Fig. 4. The differences among stations indicate the presence or absence of phytoplankton blooms. For example, the lowest values (around 0.5 μg L^{-1}) were found at stations 84 (where silicate is not depleted) and 163 located outside the various chlorophyll patches occupying the area (see satellite chlorophyll maps, Strass et al., this issue). On the other hand, highest values were found at station 174 followed by station 91 and 140 (around 2.0 μg L^{-1}), all of them diatom blooms at different development/decay stages. (Jones et al., this issue; Hoppe et al., this issue; Cheah et al., this issue). Finally, intermediate levels (around 1 μg L^{-1}) were found at station 143, close to South Georgia, where recent inputs of iron and nutrients from the island created a bloom in its initial stages.

3.4 POC and DOC

Vertical profiles of particulate organic carbon (POC; μg L^{-1}) and dissolved organic carbon (DOC; μg L^{-1}) are presented in Figure 5. POC levels in surface waters varied between 50 and 350 μg L^{-1} with significant concentrations down to 120 m above the deep background concentration. The highest values in the first 100 m of the water

column were found at stations 163, 140 and 174 (phytoplankton bloom stations) with lower values at stations 84 (south of the SPF) and 143 (vicinity of South Georgia). Values were similar among stations and around 40 µg L^{-1} in deep waters.

DOC values were quite similar among stations and around 600 µg L^{-1} with the exception of station 140 (later stages of the 12º W bloom) that showed a surface value around 850 µg L^{-1} and station 91 with values close to 700 µmol L^{-1} at different depths down to 120 m. Please note that values for st. 84 are the ones measured in a closer station with the same conditions as DOC was not measured at station 84 during the cruise.

3.5 Mercury and methylmercury

The range of total dissolved mercury (HgT) and methylmercury (MeHg) concentrations (ng L^{-1}) for each sampling station are presented in Table 1.

The average HgT concentrations obtained for stations. 91, 140, 143, 163 and 174 (filtered water) was 0.71±0.35 ng L^{-1} (range: 0.21-1.23 ng L^{-1}). In station 84 where unfiltered water was analysed the average HgT concentration was 1.78±0.83 ng L^{-1} (range: 0.70-3.58 ng L^{-1}).

In station 84, MeHg levels (average: 0.33±0.12 ng L^{-1}; range 0.18-0.56 ng L^{-1}) were also higher than in the other stations (average: 0.16±0.05 ng L^{-1}; range 0.09-0.31 ng L^{-1}) but again, we have to take into account that in st. 84 unfiltered water was analysed. Interestingly, once excluded the values below DL and st. 84, the difference between the lowest concentrations in MeHg at different locations and stations is not as pronounced as for HgT.

Regarding the vertical distribution (Figure 6), there is a big variability among stations. However, several common features should be highlighted. At 20 m depth, HgT concentrations were below or close to the detection limit (0.10 ng L^{-1}) in all the stations with the exception of 84 and 91. Generally, and with the exception of st. 143 and 174, levels were higher in the mixing layer than below. With respect to the vertical profiles of MeHg (Figure 6) it should be noticed the huge subsurface increase of 0.3 ng L^{-1} (150-200 m depth) at st. 84 just below the ML with the highest values among all stations (0.5-0.56 ng L^{-1}). This increase of around 0.5 ng L^{-1} MeHg is

coupled to an increase of ~1 ng L^{-1} HgT for the same station and depths. In general, and with the exception of st. 140, MeHg levels increased towards deep waters.

Finally, the percentage of MeHg with respect to total mercury oscillates in a narrow range between 10-37 % (Table 1).

4. Discussion

4.1 Mercury and methylmercury in the Atlantic sector of the Southern Ocean

Mercury biogeochemistry in the oceans is assumed to be more complex than for most of other trace elements (Cossa et al., 2011). Many processes at the ocean/atmosphere interface may occur that could change Hg levels, partitioning and speciation. In general, elemental mercury is oxidized at the atmosphere/ocean boundary layer and deposited onto the sea surface. Part of this oxidized mercury species (mainly divalent Hg, Hg^{2+}) are reduced again and re-emitted in the troposphere, or bound to mineral or organic ligands, and/or adsorbed onto phytoplankton within the photic zone (Cossa et al., 2011). In the ocean waters, Hg is transported downwards attached to particles (mainly biogenic) and can be biomethylated (implying redissolution) in the water column with rates depending on the type of microbial ecosystem associated with phytoplankton degradation (Heimbürger al., 2010), and in general with the low dissolved oxygen concentrations (e.g. Ullrich et al., 2001) commonly found in deep ocean waters. Conversely, biological and photochemical demethylation occurs concurrently, so that methylmercury concentrations reflect the balance between methylation-demethylation processes. Mercury sinking with large particles to the sediment may be involved in early diagenetic reactions that take place at the ocean-sediment interface of the abyssal sediments and constitute the final sink for Hg in the open ocean environment (Gobeil et al., 1999; Cossa et al., 2011).

In spite of these processes occurring in the world oceans the extent of each individual biogeochemical transformation depends largely on other related oceanographic variables, such as the presence of local mercury sources (natural or anthropogenic), algae blooms, ocean depths or the amount of labile organic matter (e.g., Ullrich et al.,

2001). The presence of upwelling processes is also known to affect Hg speciation in the ocean margins (e.g. Gill and Fitzgerald, 1988).

In a cruise between Tasmania and East Antarctica, Cossa and co-authors (2011) found a net HgT input to the ocean surface near the Antarctic continent from atmospheric deposition, a role of sea ice formation in the transfer of Hg enriched waters to depth, and a substantial net methylation of Hg. These findings were particularly important because in some way would explain the relatively higher values found in biota particularly in phytoplankton, the base of the marine food web (e.g. Echeveste et al., 2014).

To the best of our knowledge, and with the exception of a recent study in a transect at 40ºS published by Bratkic et al., 2016 in the south Atlantic Ocean, the work presented here is the first one published on the distribution of dissolved levels of HgT and MeHg at the surface and deeper in the water column along a transect in the Atlantic sector of the Southern Ocean.

HgT and MeHg concentrations obtained during this study are compiled in Table 2 and compared with data obtained by other authors from other oceanic areas. The concentrations of HgT found in this study are, in general, comparable to those obtained by Cossa et al. (2011) and Lamborg et al (2014). In fact, and with the exception of three stations (84, 91 and 143), HgT levels were in the same order of magnitude as those levels reported for the SO south of Tasmania (Cossa et al. 2011) and for the North and South Atlantic. At stations 84, 91 and 143 the concentrations of HgT were considerable higher reaching up to 6 times the values reported for other regions and could be attributed to local sources or lateral inputs. Concerning the higher concentrations obtained in station 84 we have to take also in consideration that the HgT was measured in unfiltered water so the presented results also have the contribution of Hg the particulate fraction.

Contrarily to what was expected in station 140 the HgT levels at the surface are not as higher as in station 91 (closest station). The explanation for this differences could be attributed to the different stages of phytoplankton bloom when the sampling occurred. While in st. 91 the bloom was at the beginning (see Table 1) in st. 140 was at the middle-end stage. It is well documented that phytoplankton can efficiently uptake dissolved Hg from water (e.g. Zhong and Wang, 2009; Faucheur et al., 2014) so it is

expected that in the middle-end stage of the bloom the amount of dissolved Hg in water would be lower. A similar behaviour among these stations (91 and 140) was observed during the same cruise in the case of dissolved iron (Laglera et al., 2013) as this element is assimilated by phytoplankton species during the development of the bloom. Cossa et al (2011) measured higher HgT levels South of Tasmania (Pacific sector of the SO) that were higher than those from other latitudes. The higher values obtained in this study were also greater than the ones obtained by Kirk et al. (2008) for the high- and sub-arctic Canada, where it is hypothesized that Hg deposition may occur in a larger scale compared to the southern hemisphere (Lamborg et al., 2002). However, if we exclude the highest concentrations obtained in stations 84, 91 and 143 our HgT levels are in the same order of magnitude reported by several authors for several world oceans (e.g. Cossa et al., 2011; Kirk at al., 2008, Hammerschimdt et al., 2012).

There is a lack of published data for MeHg concentrations for the Atlantic part of the SO, however the levels of MeHg obtained in the present study are comparable to the ones obtained by Cossa et al (2011) and higher than the ones obtained by Bratkic et al. (2016). However, in this last work the authors attributed the low levels of MeHg (some below DL) to the cruise-related longer storage of the samples, thus turning the comparison less accurate. Again, the maximum values were obtained at station 84 and this may be consequence of this water samples being unfiltered and also to the other oceanographic parameters measured at this station (low chlorophyll, upwelling of low oxygenated waters and a recently extinguished bloom (Cheah et al., this issue).

The relationship between the concentrations of HgT and MeHg for all samples is presented in Fig. 7 (open symbols correspond to station 84, unfiltered water).

In spite of lower but significant correlations (station 84: r=0.61; other stations: 0.48; $p<0.05$), Figure 7 clearly shows a positive tendency between the HgT and MeHg. These result suggest that the levels of MeHg in these waters vary with the amount of nature of the Hg present, possibly indicating that net methylation is restricted by the availability of mercury species susceptible for being methylated (e.g. chloro-complexes). However, remineralization and mixing with lateral or deep waters processes should not be excluded. The exception would be for the hypoxic waters of

the UCDW. Thus, tendencies presented above also suggests that HgT variations were mainly constituted by Hg forms susceptible of suffering methylation processes.

4.2 Vertical profiles of mercury and methylmercury

In general, particle reactive metals of no biological requirement such as Hg decrease in the ocean water column from top to bottom as a result of atmospheric Hg deposition at the ocean/atmosphere interface and removal by adsorption to sinking particles (scavenging). This behaviour was observed in several studies such as Cossa et al (2011) or Lamborg et al (2014). Accordingly, we expected to obtain similar vertical profiles of HgT and MeHg across the area of study. However, vertical profiles of both Hg and MeHg varied significantly between stations.

Since no tow-fish was available, we did not sample at the ocean/atmosphere interface due to the possible contamination by the shadow/in the wake of the research vessel. However, below 20 m depth, the variation of HgT concentrations in the water column did not follow always the above mentioned typical scavenging profile. In general, subsurface (st. 84, 91, 140 and 163) or deep (st. 143 and 174) increases of HgT have been observed in all the stations. This is suggesting the release of HgT from particles or a lateral input of dissolved Hg at these sites.

The increase of HgT (2.5 ng L^{-1}) at 100 m in station 84 (Figure 6) must be related to the surge of poor oxygenated UCDW waters together with a high downwards flux of POC (Puigcorbé et al., this issue).

At stations 91 and 163 (excluding the 20 m level at station 163) a clear decrease of HgT in the first 100 m was observed. Such pattern was also reported by other authors (e.g. Mason and Fitzgerald 1990; Cossa et al., 2011) and was attributed to the balance between Hg deposition and volatilization at the surface. Mercury volatilization may be, however, dependent of other oceanographic parameters. Total organic carbon (DOC+POC) content and their composition may retain Hg as non-photoreducible species/complexes decreasing the Hg release from surface waters by volatilization (e.g. Qureshi et al., 2009). Hg volatilization may be also influenced by the presence of other biogenic particles that may adsorb dissolved Hg decreasing the amount of Hg available for photochemistry processes at the ocean/air atmosphere interface. Thus,

the concentrations of mercury at surface waters and therefore the water profiles are strongly influenced by surface processes such as those described above.

With the exception of stations 84 and 140, dissolved MeHg concentrations increased with depth indicating a net Hg methylation in deeper waters. These results are in line with several others studies in different oceanic regimes and thought to be caused by the decrease in dissolved oxygen and the remineralization of particulate organic matter (POM) that not only provides substrate for Hg methylating bacteria but also to the release from POM of reactive Hg species such as Hg chloro- or aquo-complexes that would become available for methylation (e.g. Mason and Fitzgerald, 1990; Sunderland et al., 2009, Cossa et al., 2011; Kuss et al, 2011).

A substantial increase of MeHg levels was observed at 100-200 m at station 84 where an intrusion of Upper Circumpolar Deep Water (UCDW) where there were registered low dissolved oxygen levels and an increase of dissolved iron (Puigcorbé et al., this issue). The dissolved oxygen profile presents at 100-250 m a clear bulge to lower concentrations that must be caused by strong remineralization (Figure 2). Possibly the increase of dissolved iron is caused by the stabilization of Fe(II) concentrations always associated to hypoxic conditions (Schallenberg et al., 2015). The more anoxic oceanographic conditions observed at this station and depths are more favorable for Hg methylation (Ullrich et al., 2001) therefore explaining this enhance in dissolved MeHg between 100-200m. Above and below this depth range, MeHg levels decreased suggesting less favourable conditions for methylation and/or more favourable for demethylation. At this site the absolute concentrations of Hg (and MeHg) were higher and the remineralization ratio was lower (ca. 1.72) so these results may suggest that besides methylation conditions, probably part of the Hg was not available for methylation. Moreover, Hg produced by particle remineralization could have been complexed to more refractory dissolved organic matter. The lability of organic matter in the eastern stations should not be excluded as a factor affecting activity of methylating/demethylating bacteria.

The combination on the above factors may have important repercussions in the frame of developing oxygen minimum zones (OMZ) with the consequent enhance of mercury methylation. This OMZ are particular related to climate change since model predictions and observations reveal regional declines in oceanic dissolved oxygen,

which are probably influenced by global warming (Stramma et al., 2012). Thus, these scenarios may also pose a serious environmental risk for the increase of methylated conditions in OMZ the consequent enhance of the MeHg in ocean waters.

It should be noticed that st. 140 is the only station where an almost total depletion of MeHg was observed below 80 m. It is surprising that being the same area and having the same biogeochemical and oceanographic features as station 91, the MeHg profile is very different. During the sampling of this station, the direct radiation was ten times higher (399 W m^{-2}, Table 1) than at st. 91 what could have lead to a photoreduction and demethylation. However, UV radiation (responsible for Hg photoreduction) does not penetrate more a meter in seawater (e.g. Tedetti and Sempéré, 2006) indicating that in st. 140 the MeHg depletion may not be explained by a photochemical process. Thus, in this station other factors than the ones describe above may explain the observed data. Again the bioavailability of the Hg species for methylation or even the structure of the microbial community may be important factors for the MeHg depletion in st. 140 (e.g. Ullrich et al., 2011).

At stations 143 and 174 the highest increase of MeHg with depth was found between the surface (first 60m) and bottom waters (ratio $MeHg_{bottom}/MeHg_{top}$= 34 10 at stations 143 and 174, respectively). If we assume that this enhancement is due to high remineralization of POM with the release of reactive Hg species and consequent methylation, then high remineralization rates should also be found at these stations. Thus, remineralization rates were estimated by simply calculating the ratio between POC levels in the upper 60 m (mixing layer) and at 200 m. The obtained ratios were 1.72, 2.54, 3.91 and 3.58 for stations. 84, 140, 143 and 174 respectively. At sts. 91 and 163 the ratios were not determined since the POC levels were not determined in bottom waters. Clearly there is a positive tendency for increase of MeHg and remineralization ratios. The strong positive linear correlation between the two parameters ($r=0.78$; $p<0.05$) suggests that the increase of MeHg concentrations is related to the remineralization of POC. These numbers of remineralization rates have been confirmed using the ^{234}Th levels in the study area published in this issue (Puigcorbé et al.; Roca-Martí et al.).

4.3 Relationships of mercury and methylmercury concentrations with other oceanographic parameters

Table 3 presents the correlation matrix (95% confidence level) between the concentrations of HgT and MeHg and other environmental parameters measured during this study. Positive numbers indicate positive correlations.

Significant negative correlations were obtained between both dissolved HgT and MeHg with respect to temperature ($r=-0.665$; $p<0.05$ for HgT and $r=-0.596$; $p<0.05$ for MeHg) and POC ($r=-0.603$; $p<0.05$ for HgT and $r=-0.584$; $p<0.05$ for MeHg). The negative correlation of HgT and temperature suggests that in cooler waters the amount of dissolved Hg is higher and therefore it is expected that MeHg will be also higher, if we assume that this Hg is available for methylation. Since the biotic methylation process is expected to occur in warmer waters (higher microbial activity), our results suggests that the amount of Hg available for methylation is a key factor for having more or less MeHg in this systems.

Noticeable correlations between POC and Chl-a ($r=0.610$; $p<0.05$) and between MeHg and POC ($r=-0.584$; $p<0.05$) were observed. However, no significant correlation was observed between MeHg and Chl-a ($r=-0.374$; $p>0.05$). This might indicate that organic matter of detrital origin rather than "fresh" living phytoplankton is used by Hg-methylating bacteria as a substrate.

Strong positive correlations ($r>0.72$; $n=44$) were found between Hg/MeHg with nutrients. In the eastern stations, where Hg and MeHg levels are higher, nutrient concentrations were also higher but, as stated before, it is in these stations where MeHg proportion (a proxy of the Hg methylation rate) is lower. Nutrients (including organic nutrients), are known to increase biotic Hg methylation by the stimulation of the microbial activity (Ullrich et al., 2001). However, the same supply and availability of these compounds is also known for stimulating Hg demethylation processes by aerobic bacteria which are the main demethylating agents (Pak and Bartha, 1998; Monperrus et al., 2007). The lowest Hg methylating activity (less MeHg proportion) in the eastern stations appears again to be related to the lower content of bioavailabile organic matter at these stations. In spite of the higher concentrations of Hg at station 84, the relative amount of MeHg present at this site was lower pointing out to less favourable conditions for the methylating process, possibly related to the

nature/composition of the particulate organic matter and/or increase of demethylation. In fact, this last process should not be excluded. Besides the availability of nutrient, oxygen levels were also higher at station 84 (Figure 2) suggesting that the biodegradation of MeHg can be an important process to take into account.

5. Conclusions

The present paper reports the first dataset of total mercury and MeHg concentrations in the upper 300 m in the Atlantic sector of the Southern Ocean Contrary to previous findings in other open ocean areas, it was found a high variability even in the same sector of the Southern Ocean. This fact is explained by the huge quantity of undergoing physical and biogeochemical processes such as lateral advection, upwelling of water masses or more or less favourable conditions for methylation. Overall, we found a high correlation of MeHg concentrations with respect to HgT levels.

We want to highlight the important HgT concentrations and net methylation found at station 84 south of the SPF. In this station a clear maximum of HgT and MeHg was found at 100-200 m related to the upwelling of deep low O_2 waters.

Further studies in this area should be conducted in order to confirm this subsurface methylation bulge and MeHg-HgT biogeochemistry and cycle that could have important environmental implications.

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References

Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and loss of dissolved gaseous mercury in coastal seawater, Environmental Science and Technology, 31(12): 3606–3611.

Barkay, T., Gillman, M., Turner, R.R., 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. Applied Environmental Microbiology, NOV: 4267-4271.

Bowie A. R., Lannuzel D., Remenyi T. A., Wagener T., Lam P. J., Boyd P. W., Guieu C., Townsend A. T., Trull T. W., 2009. Biogeochemical iron budgets of the Southern Ocean south of Australia: decoupling of iron and nutrient cycles in the subantarctic zone by the summertime supply. Global Biogeochemical Cycles, 23: 1–14.

Bowman, K. L., Hammerschimdt, C.R., Lamborg, C.H., Swarr, G., 2015. Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections. Deep-Sea Research II, 116: 251-261.

Bratkic, A., Vahcic, M., Kotnik, J., Vazner, K.O., Begu, E., Woodward, E.M.S., Hoervat, M., 2016. Mercury presence and speciation in the South Atlantic Ocean along the 40ºS transect. Global Biogeochemical Cycles, 30: 1–105-119.

Cheah, W., Soppa Altenburg, M., Wiegmann, S., Laglera, L.M., Santos-Echeandia, J., Strass, V., Ossebaar, S., Hoppema, M., Klass, C., Wolf-Gladrow, D., Bracher, A., n.d. Community structure and physiological state of phytoplankton across major oceanic fronts in the Southern Ocean. Deep Sea Res. Part II Top. Stud. Oceanogr. this issue.

Chaulk A., Stern G. A., Armstrong D., Barber D. G. and Wang F., 2011. Mercury distribution and transport across the ocean–sea–ice–atmosphere interface in the Arctic ocean. Environmental Science Technology, 45(5): 1865-1872.

Covelli S., Faganeli J., Horvat M., Brambati A., 1999. Pore water distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste. Estuarine Coastal Shelf Science, 48: 415-428.

Cossa, D., Heimbürger, L-H., Lannuzelb, D., Rintoul, S.R., Butler, E.C.V., Bowie, A.R., Averty, B., Watson, R.J., Remenyi, T., 2011. Mercury in the Southern Ocean. Geochimica Cosmochimica Acta, 75: 4037-4052.

EPA 2002. U. S. EPA. Method 1630: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Washington, United States, Environmental Protection Agency

Echeveste, P., Tovar-Sánchez, A., Agusti, S., 2014. Tolerance of polar phytoplankton communities to metals. Environmental Pollution, 185, 183-195.

Faucheur, S.L., Campbell, P.G.C:, Fortin, C., Slaveycova, V.I., 2014. Interactions between mercury and phytoplankton: Speciation, bioavailability, and internal handling. Environmental toxicology and Chemistry, 33(6): 1211-1224.

Fitzgerald W. F., Lamborg C. H. and Hammerschmidt C. R., 2007. Marine biogeochemical cycling of mercury. Chemical Reviews, 107: 641–662.

Gill, G.A., Fitzgerald, W.F., 1988. Vertical mercury distributions in the ocean. Geochimica Cosmochima Acta 52(6): 1719-1728.

Gill, G.A., Bloom, N.S., Cappellino, S., Driscoll, C:T., Mason, R.P., Rudd, J.W.M., 1999. Sediment-water fluxes of mercury in Lavaca Bay, Texas. Environmental Science and Technology, 33: 747-756.

Gilmour, C., Henry E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution, 71: 131-169.

Gobeil C., Macdonald R. W. and Smith J. N., 1999. Mercury profiles in sediments of the Arctic Ocean basins. Environmental Science Technology, 33: 4194–4198.

Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. Methods of seawater analysis, 3rd ed. Wiley-VCH Verlag, Weinheim, Germany.

Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H., Visscher, P.T., 2004. Biogeochemistry of methylmercury in sediments of Long Island Sound. Marine Chemistry, 90: 31-52.

Hammerschmidt, C.R., Bowman, K.L., 2012. Vertical methylmercury distribution in the subtropical North Pacific Ocean. Marine Chemistry, 132-133: 77-82.

Heimbürger L.-E., Cossa D., Marty J.-C., Migon C., Averty B., Dufour A. and Ras J., 2010. Methyl mercury distributions in relation to the presence of nano and

picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). Geochimica Cosmochimica Acta, 74: 5549–5559.

Hoppe, C.J.M., Klaas, C., Ossebaar, S., Soppa, M.A., Cheah, W., Rost, B., Laglera L.M., Santos-Echeandía J., Wolf-Gladrow, D.A., Bracher, A., Hoppema, M., Strass, V., and Trimborn, S., *in press*. Controls of primary production in two phytoplankton blooms in the Antarctic Circumpolar Current. Deep Sea Research Part II: Topical Studies in Oceanography. This issue.

Johnels, A.G., Westermark, T., 1969. Chemical Fallout, 1st Ed. Miller, Springfield, IL kiyoura 1964.

Jones, E.M., Hoppema, M., Strass, V, Hauck, J., Salt, L., Ossebaar, S., Klaas, C., van heuven, S.M.A.C., Wolf-Gladrow, D., Stöven, T., de Baar, H.J.W., 2016. Mesoscale features create hotspots of carbon uptake in the Antarctic Circumpolar Current. Deep Sea Research Part II: Topical Studies in Oceanography. This issue.

Kirk, J.L., St. Louis, V. L., Hintelmann, H., Lehnherr, I., Else, B., Poissant, L., 2008. Methylated mercury species in marine waters of the Canadian high and sub-arctic. Environmental Science and Technology, 42, 8367-8373.

Kuss, J., Zülicke, C., Pohl, C., Schneider, B., 2011. Global biogeochemical Cycles, 25: GB3021.

Laglera, L.M., Santos-Echeandía, J., Caprara, S., Monticelli, D., 2013. Quantification of iron in seawater at the low picomolar range based on optimization of bromate/ammonia/dihydroxynaphtalene system by catalytic adsorptive cathodic stripping voltammetry. Analytical Chemistry, 85(4), 2486-2492.

Lamborg, C.H., Fitzgerald, W.F:, Damman, W.H., Benoit, J.M., Balcom, P:H:, Engstrom, D.R., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. Global Biogeochemical Cycles, 16(4), 51-151-11.

Lamborg C. H., Tseng C. M., Fitzgerald W. F., Balcom P. H. and Hammerschmidt C. R., 2003. Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with “reducible Hg” titrations. Environmental Science Technology, 37: 3316–3322

Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., Swarr, G.J., Munson, K.M., Ohnemus, D.C., Lam, P.J., Heimbürger, L-R., Rijkenberg, M.J.A., Saito, M.A., 2014. A global ocean inventory of anthropogenic mercury based on water column measurements. Nature, 512, 65-69

Laurier F. J. G., Mason R. P., Gill G. A. and Whalin L., 2004. Mercury distributions in the North Pacific Ocean – 20 years observations. Marine Chemistry, 90: 3–19

Langer, C.S., Fitzgerald, W.F., Visscher, P.T., Vandal, G.M., 2001. Biogeochemical cycling of methylmercury at Barn Island salt marsch, Stonington, CT, USA. Wetlands Ecology Management, 9: 295-310.

Lehnherr, I., St. Louis, V.L., Hintelmann, H., Kirk, J.L., 2011. Methylation of inorganic mercury in polar marine waters. Nature Geoscience, 4: 298–302.

Lorrain, A., Savoye, N., Chauvaud, L., Paulet, Y. M., and Naulet, N., 2003. Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of lowcarbonated suspended particulate material. Analytica Chimica Acta, 491, 125–133.

Mason R. P. and Fitzgerald W. F., 1990. Alkylmercury species in the Equatorial Pacific. Nature, 347: 457–459.

Mason R. P. and Fitzgerald W. F., 1993. The distribution and biogeochemical cycling of mercury in the Equatorial Pacific- Ocean. Deep-Sea Research I, 40: 1897–1924.

Mason, R. P., Laurier, F.J.G., Whalin, L., Sheu, G.R., 2003, The role of ocean-atmosphere exchange in the global mercury cycle. J. Physics IV, 107: 835–838.

Mason, R. P., Morel, F.M.M., Hemond, H.F., 1995. The role of microorganisms in elemental mercury formation in natural waters. Water, Air, Soil Pollution, 80: 775–787.

Mason, R., Rolfhus, K., Fitzgerald, W., 1998. Mercury in the North Atlantic. Marine Chemistry, 61(1–2): 37–53.

Mason, R.P., Lawson, N.M., Lawrence, A.L., Leaner, J.J., Lee, J.G., Sheu, G.R., 1999. Mercury in Chesapeake Bay. Marine Chemistry, 65: 77-96.

Mason R. P. and Sullivan K. A., 1999. The distribution and speciation of mercury in the South and equatorial Atlantic. Deep-Sea Research II, 46: 937–956.

Mason R. P., Lawson N. M. and Sheu G.-R., 2001. Mercury in the Atlantic Ocean: factors controlling air–sea exchange of mercury and its distribution in the upper waters. Deep-Sea Research II, 48: 2829–2853.

Mason, R.P., Benoit, J.M., 2003. Organomercury compounds in the environment. In P. Graig Organometallic compounds in the environment, pp. 57-99. Wiley, ,West Sussex, UK.

Mason R. P. and Gill G. A., 2005. Mercury in the marine environment. In Mercury Sources, Measurements, Cycles, and Effects. Short Course, Series Volume 34 (eds. M. B. Parsons and J. B. Percival). Mineralogical Association of Canada, Halifax, Nova Scotia, Canada: pp. 179–216.

Mauro, J.B.N., Guimarães, J.R.D., Melamed, R. 1999. Mercury methylation in a tropical macrophyte: influence of abiotic parameters. Applied Organometallic Chemistry, 13: 631-636.

Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. Marine Chemistry 107: 49-63.

Moreno, F.N., Anderson, C.W.N., Stewart, R.B., Robinson, B.H. 2005. Mercury volatilization and phytoextraction from base-metal mine tailings. Environmental Pollution, 136: 341-352.

Pacyna, E.G., Pacyna, J.M., Pirrone, M., 2001. European emissions of atmospheric mercury from antrophogenic sources in 1995. Atmospheric Environment 35: 2987-2996.

Pak, K-R., Bartha, R., 1998. Mercury Methylation and Demethylation in Anoxic Lake Sediments and by Strictly Anaerobic Bacteria. Applied and Environmental Microbiology 64(3): 1013-1017.

Puigcorbé, V., Roca-Martí, M., Masqué, P., Benitez-Nelson, C.R., v. d. Loeff , M.R., Laglera, L.M., Bracher, A. Cheah, W.,Strass, V., Hoppema, M., Santos-Echeandía, J.,

Hunt, B.P.V, Pakhomov, E.A., Klaas, C. 2016. Particulate organic carbon export across the Antarctic Circumpolar Current at 10ºE: Differences north and south of the Antarctic Polar Front. Deep Sea Research Part II: Topical Studies in Oceanography This Issue.

Qureshi, A., O'Driscoll, N.J., MacLeod, M., Neuhold, Y-M., Hungerbühler, K., 2009. Photoreactions of mercury in surface ocean water: gross reaction kinetics and possible pathways. Environmental Science and Technology 44(2): 644-649.

Roca-Martí, M., Puigcorbé, V., Iversen, M.H., van der Loeff, M.R., Klaas, C., Cheah, W., Bracher, A., Masqué, P. 2016. High particulate organic carbon export during the decline of a vast diatom bloom in the Atlantic sector of the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography This Issue.

Rolfhus, K. R., Fitzgerald, W.F., 2001. The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY. Geochimica Cosmochimica Acta, 65(3): 407–418.

Schallenberg, C., Davidson, A.B., Simpson, K.G., Miller, L.A., Cullen, J.T., 2015. Iron(II) variability in the northeast subarctic Pacific Ocean. Mar. Chem. 177, Part 1, 33-44.

Stramma, L., Prince, E.D., Schmidtko, S., Luo, J., Hoolihan, J.P., Visbeck M., Wallace, D.W.R., Brandt, P., Körtzinger, !., 2012. Expansion of oxygen minimum zones may reduce available habitat for tropical pelagic fishes. Nature Climate Change 2: 33–37

Strass, V. H., H. Leach, H. Prandke, M. Donnelly, A. U. Bracher and D. A.Wolf-Gladrow, 2016. The physical environmental conditions of biogeochemical differences along the ACC in the Atlantic Sector during late austral summer 2012. This Issue.

Strode, S., Jaegle, L., Selin, N., Jacob, D., Park, R., Yantosca, R., Mason, R., Slemr, F., 2007, Air-sea exchange in the global mercury cycle. Global Biogeochemical Cycles, 21, GB1017.

Sunderland E. M., Krabbenhoft D. P., Moreau J. W., Strode S. A. and Landing W. M., 2009. Mercury sources, distribution, and bioavailability in the North Pacific Ocean: insights from data and models. Global Biogeochemical Cycles 23, 1-15.

Tedetti, M., Sempéré, R., 2006. Penetration of ultraviolet radiation in the marine environment. A review. Photochemistry and Photobiology, 82(2): 389-397.

Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in aquatic environment: a review of factors affecting methylation. Critical Reviews in Environmental Science and Technology, 31(3): 241-293.

Zhang, Y., Jaeglé. L., Thompson, L., 2014. Natural biogeochemical cycle of mercury in a global three-dimensional ocean tracer-model. Global Biogeochemical Cycles, 28, 553-570.

Zhong, H., Wang, W-X., 2009. Controls of dissolved organic Matter and chloride on mercury uptake by a marine diatom. Environmental Science and Technology, 43(23): 8998-9003.

Figure and Table Captions

Figure 1. Study area with the sampling stations.

Figure 2. Vertical profiles of salinity (psu), temperature (ºC) and dissolved oxygen (µmol kg^{-1}) at each sampling station.

Figure 3. Vertical profiles of nitrite, nitrate, phosphate and silicate concentrations (µmol L^{-1}) at each sampling station.

Figure 4. Vertical profiles of *chlorophyll a* (µg L^{-1}) at each sampling station.

Figure 5. Vertical profiles of particulate organic carbon (POC, µg L^{-1}) and dissolved organic carbon (DOC, µg L^{-1}) at each sampling station.

Figure 6. Vertical profiles of total dissolved Hg and MeHg (ng L^{-1}) in the six sampling stations. Note the difference in the y-axis scale for station 84 (500 m instead of 300 m depth). Values below detection limit have been ploted with the values of the detection limit (0.1 ng L^{-1} for HgT and 0.02 ng L^{-1} for MeHg) and are shown with a grey dot (dark for HgT and light for MeHg).

Figure 7. Relationship between HgT and MeHg concentrations (ng L^{-1}) obtained for all samples (samples with MeHg below detection limit (DL) were excluded). White dots correspond to station 84 (unfiltered water).

Table 1. Total dissolved Hg and MeHg concentrations (ng L^{-1}) at all stations sampled during the Eddy Pump cruise, depth range 0-300 m.

Table 2. Concentrations of HgT and MeHg (ng L^{-1}) obtained in this study and in other similar studies for the Atlantic and Southern Ocean waters.

Table 3. Correlation matrix between Hg, MeHg and ancillary parameters measured at all the stations and depths. Positive numbers indicate positive correlations. Figures in bold when the correlation is statistically significative ($p<0.05$).

Mercury and methylmercury in the Atlantic sector of the Southern Ocean

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Abstract

Oceans constitute one of the most important reservoirs for mercury. In order to provide a first insight into the concentrations of Hg species in the Atlantic sector of the Southern Ocean a sampling campaign was carried out south of the Polar Front.

Water samples taken at discrete depths from the surface down to 300 m at six stations were analysed for total Hg (HgT), methylmercury (MeHg) and other interpretative parameters such as salinity, temperature, dissolved and particulate organic carbon, dissolved oxygen, chlorophyll and inorganic nutrients.

Results showed a high spatial variability in the concentrations of HgT and MeHg. HgT (0.93±0.69 ng L^{-1}) and MeHg (0.26±0.12 ng L^{-1}) levels were similar or higher than those reported in previous works in high latitude studies. The highest values were found at a location (-53º, 10ºE) south of the South Polar Front, an area of strong gradients caused by the mixing of different water masses. Vertical profiles showed a great variability even for those stations sampled at the same location or an area dominated by the same oceanographic features. A decrease of HgT and a consequent increase in MeHg with depth was observed in some sites, suggesting the occurrence of Hg-methylation process, while at other stations, a concurrent decrease or increase of both mercury species was observed. In spite of these differences, an overall positive correlation between HgT and MeHg was observed. Differences between vertical profiles of Hg species were attributed to favourable environmental conditions for Hg methylation. The highest proportion of MeHg (% of HgT) was observed in sites with low dissolved oxygen or highest estimated remineralization rates.

The results obtained in this study show that the Hg distribution and speciation in the Atlantic sector of the SO is comparable (or in some sites higher) to the ones published for the other open ocean regions. However, the concentrations of MeHg in this area are more dependent on the environmental conditions than on the total concentration of Hg present in the water.

Keywords: mercury, methylmercury, Atlantic sector, Southern Ocean, Eddy Pump cruise

1. Introduction

Mercury (Hg) is a globally distributed pollutant that cycles between air, water, sediment, soil and organisms (Moreno et al., 2005) and is considered by the United Nations Environmental Program (UNEP) as a pollutant of great concern. Its presence in the environment is increased due to anthropogenic sources, and can create fatal health issues. Although anthropogenic emissions of Hg have been reduced by half in the last decades (Pacyna et al., 2001), ongoing contamination is still a worldwide problem. The conversion of inorganic Hg into methylmercury (MeHg; CH_3-Hg^+), a strong neurotoxin, is a critical step in its fate and toxicity. Interest in MeHg as an environmental contaminant first arose in the 1960's with reports of alkylmercury poisoning of marine life and humans in Japan, and birds and marine life in Sweden (Kiyoura, 1964; Johnels and Westermark, 1969). The net MeHg concentrations result from the balance between methylation and demethylation processes, which are not completely understood (Mason and Benoit, 2003). The most important factors influencing biological methylation are the availability of inorganic mercury and the nature of the microbial community (Mauro et al, 1999; Ullrich et al., 2001) modulated by physical and chemical parameters such as temperature, pH, salinity, organic carbon, and redox potential (Gilmour and Henry, 1991; Barkay et al., 1997; Ullrich et al., 2001; Mason and Benoit, 2003). Despite the paucity of information concerning sources, in situ production, biogeochemistry and bioaccumulation of MeHg in marine organisms, sediments appear as potentially significant sources of MeHg to food webs in the coastal zone (Mason et al., 1999; Gill et al., 1999; Covelli et al,. 1999; Langer et al., 2001; Hammerschmidt et al., 2004) and to the open ocean via hydrological or biological transport.

The ocean plays a central role in global mercury biogeochemical cycling. Within the ocean, Hg cycles among elemental (Hg^0), inorganic (Hg^{2+}), MeHg, dimethylmercury (DMHg), and particle-bound (Hg_P) forms (Mason and Fitzgerald, 1993). Atmospheric wet and dry depositions supply Hg to the surface ocean. In the mixed layer, Hg(II) may be (photo)reduced to Hg^0 and then re-emitted to the atmosphere (Qureshi et al., 2009). Hg(II) can also be adsorbed onto suspended organic-rich particulate matter (Hg_P). Deeper ocean remineralization of sinking particulate matter converts Hg_P to

dissolved Hg(II), thus resupplying Hg to the dissolved pool at depth (Mason et al., 1995; Amyot et al., 1997; Rolfhus and Fitzgerald, 2001; Fitzgerald et al., 2007, Strode et al., 2010). The hypoxic (low-oxygen) zone in the subsurface ocean is hypothesized to be an area of optimum biological methylation/demethylation processes (Sunderland et al., 2009; Lehnherr et al., 2011).

Burial of Hg_P in marine sediments is the terminal sink for Hg (Lamborg et al., 2003). Vertical profiles in ocean waters generally contain the signatures of three different processes:

i. in the mixed layer, total mercury (HgT) concentrations can exhibit a maximum or minimum relative to subsurface waters depending on the relative roles of sources (atmospheric deposition and upwelling of Hg-rich waters) and sinks (air-sea gas exchange and scavenging onto particles) (e.g. Zhang et al., 2014);
ii. the thermocline/intermediate waters (between the bottom of the mixed layer down to 1000 m depth) often display a local maximum in HgT (Zhang et al., 2014). This maximum has been interpreted as a Hg release from remineralization of sinking particulate matter. This maximum can also be interpreted as an anthropogenic signal from high-deposition regions through isopycnal transport or adsorption onto sinking particulate matter (Mason et al., 1998; Mason and Sullivan, 1999; Fitzgerald et al., 2007; Strode et al., 2010).
iii. in the deep ocean (>1000 m), HgT concentrations are relatively constant and sometimes slightly increase with depth (e.g., Laurier et al., 2004; Lamborg et al., 2012).

Many studies have been published about the Hg cycling in the world oceans (see references above) although, and with the exception of the biological compartments, less attention has been given to the Southern Ocean (SO). The first paper aiming to better understand the “abiotic” mercury cycle in the Southern Ocean was published by Cossa et al. (2011). In a scientific cruise between Tasmania and Antarctica, Cossa et al. (2011) found that Hg_T concentrations in water samples were comparable to recent measurements made in other parts of the world's oceans, however the Hg species distribution suggested distinct features in the SO Hg cycle: a net atmospheric Hg

deposition on surface water near the ice edge, an Hg enrichment in brine during sea ice formation, and a net methylation of Hg.

The work presented here contributes to the scientific efforts to understand the Hg cycling in the SO. During a RV Polarstern cruise in the Atlantic sector of the SO, several water profiles down to 300 m were sampled and analysed for total Hg, MeHg and other interpretative parameters (e.g. salinity, temperature, dissolved and particulate organic carbon, etc). The aim of this work is therefore to provide a first insight into the concentrations of Hg species in this area and to understand the processes responsible for their distribution, partitioning and speciation.

2. Material and Methods

2.1. Sampling

Sampling was carried out as part of the RV Polarstern "Eddy-Pump - ANTXXVIII/3" cruise along a longitudinal transect in the Atlantic sector of the Southern Ocean around latitude 50° S between January and March 2012 (Fig. 1).

Four different areas were sampled for Hg from east to west (see Table 1 for a more detailed position): in the east station 84 was located south of the Southern Polar Front (SPF) at 10ºE, two stations were located in the central Atlantic sector (stations 91 and 140) between the SPF and the Antarctic Polar Front (APF) where a large open ocean diatom bloom was investigated (up to 2 μg chl-a L^{-1}), the third region was further to the west (stations 163 and 174) between the APF and SPF at the North end of the South Georgia basin. Finally, station 143 was located close to South Georgia in the SPF (receiving iron inputs from the vicinity of the island, data not published). Details of the addressing fronts, their locations and biogeochemical features are provided in this issue (Strass et al.; Hope et al.; Puigcorbé et al.). The first station (st. 84) was characterized by low plankton biomass (<0.5 μg chl-a L^{-1}) in the euphotic layer (caused by a bloom in its declining stage; Cheah et al., this issue) and the surge of high iron/low oxygen waters of the Upper Circumpolar Deep Water (UCDW) which effect can be tracked up to 150 m deep (Puigcorbé et al., this issue). The second and third areas presented different development stages of a phytoplankton bloom. The last

area, close to South Georgia, provides information on the influence of the "Island effect" on the levels and biogeochemical cycle of Hg in these waters.

Profiles of temperature, salinity and pressure were measured with a Seabird SBE 911plus CTD (conductivity-temperature-density; Strass et al., this issue). Samples for chlorophyll a, DOC, POC and macronutrients (nitrate+nitrite, phosphate, silicic acid) analyses were collected from Niskin bottles attached to the CTD.

Since solar radiation may change and reduce some forms of mercury, direct solar radiation data have been included in Table 1 for each station during the sampling time (LI-COR 192SA light sensor). Half of the stations (84, 143 and 163) were sampled at night, while the rest of the stations showed a radiation range between 34-795 W m^{-2}.

All material and equipment used for mercury (and MeHg) storage and analysis (PTFE-Nalgene) were previously acid decontaminated. Briefly all material was washed with ultrapure water (Milli-Q Elemental System – 18.2 MΩ cm), two times with a solution of HCl (Suprapur-Merck) 20% (v/v) and after, rinsed again with Milli-Q and submerged in a HNO_3 (Hg-free) solution at 30% (v/v) for a week. Finally, the material was washed several times with Milli-Q water. All sampling flasks were filled with a solution of 1% HNO_3 (Hg-free) solution until sampling.

Samples for Hg and MeHg analyses were collected from the upper 300 m of the water column by means of 8 metal-free GOFLO bottles attached to a Kevlar line. With the exception of station 84 (unfiltered samples) all other samples were immediately filtered online (0.2 μm) by means of filtration sterile capsules (Sartobran 300) and collected in PTFE bottles (Nalgene). Samples for the determination of dissolved iron were collected in LDPE bottles (VWR) from the same GOFLO bottles used to collect Hg samples.

2.2. Analysis

Macronutrients

Macronutrients (PO_4^{3-}, $Si(OH)_4$, NO^{3-} and NO^{2-}) were measured onboard using a Technicon TRAACS800 autoalyzer (SealAnalytical). Details about analytical

protocols can be found in (Hoppe et al., in press) and elsewhere (Grasshoff et al., 1999).

Chlorophyll *a*

Chlorophyll a (Chl a) determinations were carried out using a 10-AU fluorometer (Turner). A more detailed description of the pretreatment and analysis procedure can be found in (Hoppe et al.).

Dissolved organic carbon (DOC) and Particulate organic carbon (POC)

Samples (~60 mL) for DOC analysis were filtered through pre-combusted GF/F filters using an HCl-cleaned glass filtration unit. The procedure was repeated 3 times for each sample in order to rinse the vials and the filtration unit, keeping the last filtrate for analysis. The final filtrate was collected directly into HCl-rinsed plastic (HDPE) bottles and frozen (-20°C) for further analysis on land. DOC was determined by high temperature catalytic oxidation (TOC-VCPN analyzer, Shimadzu) (Skoog et al., 1997). For external calibration potassium hydrogen phthalate (KHP, Merck) was used. Aliquots of the methanol extracts (50 mL) from the SPE samples were evaporated under N_2 gas flow to complete dryness and subsequently redissolved in 6.5 mL ultrapure water for DOC analysis (SPE-DOC). All samples were acidified (0.1 M HCl suprapur, Merck) and purged with O_2 for 5 min. Performance of the instrument was recorded by daily analysis of in-lab KHPstandard solutions and reference samples (deep sea reference, DSR, Hansell research lab). Repeatability of the DSR was >95% (ns = 42) and average blank values (water from the ship's MilliQ system processed as the the field samples) was 1.0 µM (± 2 µM std).

Samples for particulate organic carbon (POC) were filtered onto pre-combusted (15h, 500 °C) glass fibre filters (GF/F, Whatman). Filters were stored at -20 °C and processed according to Lorrain et al. (2003). Analyses were performed using a CHNS-O elemental analyser (EuroEA3000, HEKAtech).

Total mercury and methylmercury

After water collection samples were preserved with 7.5 mL (per 40 mL sample) of 33% HCl (Merck, Hg-free) for total mercury determinations and at 0.5% HCl for methylmercury.

Total Hg was determined applying the EPA 1631B method (EPA, 2002), using a PSA Merlin system by CV-AFS. Briefly, 1mL of bromine monochloride (BrCl) was added to the sample followed by the addition of 100µL of hydroxylamine solution to reduce the excess of BrCl. Total mercury was then determined by Cold Vapour Atomic Fluorescence (CV-AFS) Spectroscopy in PSA Millenium Merlin equipment using $SnCl_2$ as a reducing agent. Hg quantification was made using a calibration curve obtained by measuring several standards (0-30 ngL^{-1}) prepared by an adequate dilution of a 1000 ppm Merck standard solution.

Methylmercury concentrations were determined by GC-CV-AFS using automatic MERX equipment manufactured by Brooks Rand Labs, by distillation, aqueous phase ethylation buffered to pH 4.9 with an acetate buffer, purge and trap and separation by Gas Chromatography. Finally, Hg species were reduced to Hg^0 and detected by AFS. Concentrations were determined using the standard addition method. A stock standard solution of MeHg was prepared from the solid (MeHgCl – Aldrich) by dissolving the exact amount of compound in ethanol. This stock solution was used to spike the water samples before the extractions following the methodology described in Canário et al., (2006).

QA/QC control for mercury measurements

Analytical quality control was performed with calibrations and blanks on a daily basis and sample replicates.

Field blanks (n=12), reagents blanks (n=12), and laboratory blanks (n=8) were always used during the all analytical procedure. With the exception of two laboratory blanks (HgT) the blanks fluorescence signals were always equal or below the detection limit, calculated as 3 times the standard deviation of the blank average. We had a particularly concern by doing all blanks using the same reagents that were used in the field.

Certified reference materials were used tto access the accuracy of our results. Thus, BCR 579 (European Commission - Hg in sea water - certified: 1.9±0.5 ng L^{-1}; obtained: 1.6±0.3 ng L^{-1}, n=14) and ORMS-5 (NRCC Canada - Hg in river water - certified: 26.2±1.3 ng L^{-1}; obtained: 25.7±0.8 ng L^{-1}, n=14) diluted 10 times with Milli-Q water at 1% HNO_3 (Hg-free) were analysed for this purpose. The obtained

and certified values were not statistically different (t-test, 95% confidence level) (Miller and Miller, 2010).

Analytical recoveries of both Hg and MeHg were determined using the spike technique as ranged from 90 to 109 % for Hg and for MeHg from 92 to 103 %. Replicate samples were also used to assess variability of the data. The limits of detection (LOD) were calculated as three times the standard deviation from blanks repeated in every 20 samples to evaluate cross contamination and if the equipment were operating at the same conditions: for dissolved fraction Hg 0.10±0.015 ng L^{-1} and MeHg 0.02±0.0002 ng L^{-1}; repeatability was less than 6.0 % (n = 8), expressed as a percentage relative standard deviation (Miller and Miller, 2010).

3. Results

3.1 Salinity, temperature and dissolved oxygen

The vertical profiles of salinity (psu), temperature (ºC) and dissolved oxygen (μmol kg^{-1}) obtained for all the sites are presented in Fig. 2.

Salinity values ranged between 33.67-34.67 with lower values in the surface mixed layer (ML) (Table 1) and increased with depth at all the stations. Station 84, located south of the SPF, showed the highest salinity below the mixed layer, followed by the station 143. In the case of the mixed layer, salinity was also highest at station 84.

All stations showed a subsurface temperature minimum with temperatures below 2°C, indicative of Antarctic Winter Water, and that all were located south of the APF. The lowest values were found at station 84, followed by stations 143, 140 and 91 (in this order) with the highest temperatures at stations 163 and 174 (between 5 and 6°C). Below 200 meters, temperature values were similar among stations and close to 2°C.

The highest dissolved oxygen concentrations in the first 100 meters were found at station 84 followed by stations 91, 140 and 143 with the lowest dissolved oxygen levels found at stations 163 and 174. Below 100 m depth the trend changed with lowest oxygen concentrations at station 84 followed by station 143 and 140 and highest values at stations 91, 163 and 174.

In summary, the effect of the surging UCDW waters gave station 84 quite different properties from the rest of the stations, i.e.: lower temperature in the ML and higher

salinity and lower dissolved oxygen concentrations below the ML compared to the rest of the stations.

3.2 Nutrients

Nutrients vertical profiles for all sampling stations are presented in Figure 3. The highest values for all nutrients in surface waters (nitrite, nitrate, phosphate and silicate) were found at station 84 followed by stations 91 and 140 with the lowest values at stations 163 and 174. Silicate values in the ML were high at station 84, while at all other stations silicate has been depleted or brought close to limiting concentrations for diatom growth. Nutrient levels showed similar values at depth with the exception of silicate that remained higher at st. 84 as compared to the other stations caused by the surging of deep waters.

3.3 Chlorophyll *a*

The vertical profiles of chlorophyll (μg L^{-1}) in all sites are presented in Fig. 4. The differences among stations indicate the presence or absence of phytoplankton blooms. For example, the lowest values (around 0.5 μg L^{-1}) were found at stations 84 (where silicate is not depleted) and 163 located outside the various chlorophyll patches occupying the area (see satellite chlorophyll maps, Strass et al., this issue). On the other hand, highest values were found at station 174 followed by station 91 and 140 (around 2.0 μg L^{-1}), all of them diatom blooms at different development/decay stages. (Jones et al., this issue; Hoppe et al., this issue; Cheah et al., this issue). Finally, intermediate levels (around 1 μg L^{-1}) were found at station 143, close to South Georgia, where recent inputs of iron and nutrients from the island created a bloom in its initial stages.

3.4 POC and DOC

Vertical profiles of particulate organic carbon (POC; μg L^{-1}) and dissolved organic carbon (DOC; μg L^{-1}) are presented in Figure 5. POC levels in surface waters varied between 50 and 350 μg L^{-1} with significant concentrations down to 120 m above the deep background concentration. The highest values in the first 100 m of the water

column were found at stations 163, 140 and 174 (phytoplankton bloom stations) with lower values at stations 84 (south of the SPF) and 143 (vicinity of South Georgia). Values were similar among stations and around 40 µg L^{-1} in deep waters.

DOC values were quite similar among stations and around 600 µg L^{-1} with the exception of station 140 (later stages of the 12º W bloom) that showed a surface value around 850 µg L^{-1} and station 91 with values close to 700 µmol L^{-1} at different depths down to 120 m. Please note that values for st. 84 are the ones measured in a closer station with the same conditions as DOC was not measured at station 84 during the cruise.

3.5 Mercury and methylmercury

The range of total dissolved mercury (HgT) and methylmercury (MeHg) concentrations (ng L^{-1}) for each sampling station are presented in Table 1.

The average HgT concentrations obtained for stations. 91, 140, 143, 163 and 174 (filtered water) was 0.71±0.35 ng L^{-1} (range: 0.21-1.23 ng L^{-1}). In station 84 where unfiltered water was analysed the average HgT concentration was 1.78±0.83 ng L^{-1} (range: 0.70-3.58 ng L^{-1}).

In station 84, MeHg levels (average: 0.33±0.12 ng L^{-1}; range 0.18-0.56 ng L^{-1}) were also higher than in the other stations (average: 0.16±0.05 ng L^{-1}; range 0.09-0.31 ng L^{-1}) but again, we have to take into account that in st. 84 unfiltered water was analysed. Interestingly, once excluded the values below DL and st. 84, the difference between the lowest concentrations in MeHg at different locations and stations is not as pronounced as for HgT.

Regarding the vertical distribution (Figure 6), there is a big variability among stations. However, several common features should be highlighted. At 20 m depth, HgT concentrations were below or close to the detection limit (0.10 ng L^{-1}) in all the stations with the exception of 84 and 91. Generally, and with the exception of st. 143 and 174, levels were higher in the mixing layer than below. With respect to the vertical profiles of MeHg (Figure 6) it should be noticed the huge subsurface increase of 0.3 ng L^{-1} (150-200 m depth) at st. 84 just below the ML with the highest values among all stations (0.5-0.56 ng L^{-1}). This increase of around 0.5 ng L^{-1} MeHg is

coupled to an increase of ~1 ng L^{-1} HgT for the same station and depths. In general, and with the exception of st. 140, MeHg levels increased towards deep waters.

Finally, the percentage of MeHg with respect to total mercury oscillates in a narrow range between 10-37 % (Table 1).

4. Discussion

4.1 Mercury and methylmercury in the Atlantic sector of the Southern Ocean

Mercury biogeochemistry in the oceans is assumed to be more complex than for most of other trace elements (Cossa et al., 2011). Many processes at the ocean/atmosphere interface may occur that could change Hg levels, partitioning and speciation. In general, elemental mercury is oxidized at the atmosphere/ocean boundary layer and deposited onto the sea surface. Part of this oxidized mercury species (mainly divalent Hg, Hg^{2+}) are reduced again and re-emitted in the troposphere, or bound to mineral or organic ligands, and/or adsorbed onto phytoplankton within the photic zone (Cossa et al., 2011). In the ocean waters, Hg is transported downwards attached to particles (mainly biogenic) and can be biomethylated (implying redissolution) in the water column with rates depending on the type of microbial ecosystem associated with phytoplankton degradation (Heimbürger al., 2010), and in general with the low dissolved oxygen concentrations (e.g. Ullrich et al., 2001) commonly found in deep ocean waters. Conversely, biological and photochemical demethylation occurs concurrently, so that methylmercury concentrations reflect the balance between methylation-demethylation processes. Mercury sinking with large particles to the sediment may be involved in early diagenetic reactions that take place at the ocean-sediment interface of the abyssal sediments and constitute the final sink for Hg in the open ocean environment (Gobeil et al., 1999; Cossa et al., 2011).

In spite of these processes occurring in the world oceans the extent of each individual biogeochemical transformation depends largely on other related oceanographic variables, such as the presence of local mercury sources (natural or anthropogenic), algae blooms, ocean depths or the amount of labile organic matter (e.g., Ullrich et al.,

2001). The presence of upwelling processes is also known to affect Hg speciation in the ocean margins (e.g. Gill and Fitzgerald, 1988).

In a cruise between Tasmania and East Antarctica, Cossa and co-authors (2011) found a net HgT input to the ocean surface near the Antarctic continent from atmospheric deposition, a role of sea ice formation in the transfer of Hg enriched waters to depth, and a substantial net methylation of Hg. These findings were particularly important because in some way would explain the relatively higher values found in biota particularly in phytoplankton, the base of the marine food web (e.g. Echeveste et al., 2014).

To the best of our knowledge, and with the exception of a recent study in a transect at 40ºS published by Bratkic et al., 2016 in the south Atlantic Ocean, the work presented here is the first one published on the distribution of dissolved levels of HgT and MeHg at the surface and deeper in the water column along a transect in the Atlantic sector of the Southern Ocean.

HgT and MeHg concentrations obtained during this study are compiled in Table 2 and compared with data obtained by other authors from other oceanic areas. The concentrations of HgT found in this study are, in general, comparable to those obtained by Cossa et al. (2011) and Lamborg et al (2014). In fact, and with the exception of three stations (84, 91 and 143), HgT levels were in the same order of magnitude as those levels reported for the SO south of Tasmania (Cossa et al. 2011) and for the North and South Atlantic. At stations 84, 91 and 143 the concentrations of HgT were considerable higher reaching up to 6 times the values reported for other regions and could be attributed to local sources or lateral inputs. Concerning the higher concentrations obtained in station 84 we have to take also in consideration that the HgT was measured in unfiltered water so the presented results also have the contribution of Hg the particulate fraction.

Contrarily to what was expected in station 140 the HgT levels at the surface are not as higher as in station 91 (closest station). The explanation for this differences could be attributed to the different stages of phytoplankton bloom when the sampling occurred. While in st. 91 the bloom was at the beginning (see Table 1) in st. 140 was at the middle-end stage. It is well documented that phytoplankton can efficiently uptake dissolved Hg from water (e.g. Zhong and Wang, 2009; Faucheur et al., 2014) so it is

expected that in the middle-end stage of the bloom the amount of dissolved Hg in water would be lower. A similar behaviour among these stations (91 and 140) was observed during the same cruise in the case of dissolved iron (Laglera et al., 2013) as this element is assimilated by phytoplankton species during the development of the bloom. Cossa et al (2011) measured higher HgT levels South of Tasmania (Pacific sector of the SO) that were higher than those from other latitudes. The higher values obtained in this study were also greater than the ones obtained by Kirk et al. (2008) for the high- and sub-arctic Canada, where it is hypothesized that Hg deposition may occur in a larger scale compared to the southern hemisphere (Lamborg et al., 2002). However, if we exclude the highest concentrations obtained in stations 84, 91 and 143 our HgT levels are in the same order of magnitude reported by several authors for several world oceans (e.g. Cossa et al., 2011; Kirk at al., 2008, Hammerschimdt et al., 2012).

There is a lack of published data for MeHg concentrations for the Atlantic part of the SO, however the levels of MeHg obtained in the present study are comparable to the ones obtained by Cossa et al (2011) and higher than the ones obtained by Bratkic et al. (2016). However, in this last work the authors attributed the low levels of MeHg (some below DL) to the cruise-related longer storage of the samples, thus turning the comparison less accurate. Again, the maximum values were obtained at station 84 and this may be consequence of this water samples being unfiltered and also to the other oceanographic parameters measured at this station (low chlorophyll, upwelling of low oxygenated waters and a recently extinguished bloom (Cheah et al., this issue).

The relationship between the concentrations of HgT and MeHg for all samples is presented in Fig. 7 (open symbols correspond to station 84, unfiltered water).

In spite of lower but significant correlations (station 84: $r=0.61$; other stations: 0.48; $p<0.05$), Figure 7 clearly shows a positive tendency between the HgT and MeHg. These result suggest that the levels of MeHg in these waters vary with the amount of nature of the Hg present, possibly indicating that net methylation is restricted by the availability of mercury species susceptible for being methylated (e.g. chloro-complexes). However, remineralization and mixing with lateral or deep waters processes should not be excluded. The exception would be for the hypoxic waters of

the UCDW. Thus, tendencies presented above also suggests that HgT variations were mainly constituted by Hg forms susceptible of suffering methylation processes.

4.2 Vertical profiles of mercury and methylmercury

In general, particle reactive metals of no biological requirement such as Hg decrease in the ocean water column from top to bottom as a result of atmospheric Hg deposition at the ocean/atmosphere interface and removal by adsorption to sinking particles (scavenging). This behaviour was observed in several studies such as Cossa et al (2011) or Lamborg et al (2014). Accordingly, we expected to obtain similar vertical profiles of HgT and MeHg across the area of study. However, vertical profiles of both Hg and MeHg varied significantly between stations.

Since no tow-fish was available, we did not sample at the ocean/atmosphere interface due to the possible contamination by the shadow/in the wake of the research vessel. However, below 20 m depth, the variation of HgT concentrations in the water column did not follow always the above mentioned typical scavenging profile. In general, subsurface (st. 84, 91, 140 and 163) or deep (st. 143 and 174) increases of HgT have been observed in all the stations. This is suggesting the release of HgT from particles or a lateral input of dissolved Hg at these sites.

The increase of HgT (2.5 ng L^{-1}) at 100 m in station 84 (Figure 6) must be related to the surge of poor oxygenated UCDW waters together with a high downwards flux of POC (Puigcorbé et al., this issue).

At stations 91 and 163 (excluding the 20 m level at station 163) a clear decrease of HgT in the first 100 m was observed. Such pattern was also reported by other authors (e.g. Mason and Fitzgerald 1990; Cossa et al., 2011) and was attributed to the balance between Hg deposition and volatilization at the surface. Mercury volatilization may be, however, dependent of other oceanographic parameters. Total organic carbon (DOC+POC) content and their composition may retain Hg as non-photoreducible species/complexes decreasing the Hg release from surface waters by volatilization (e.g. Qureshi et al., 2009). Hg volatilization may be also influenced by the presence of other biogenic particles that may adsorb dissolved Hg decreasing the amount of Hg available for photochemistry processes at the ocean/air atmosphere interface. Thus,

the concentrations of mercury at surface waters and therefore the water profiles are strongly influenced by surface processes such as those described above.

With the exception of stations 84 and 140, dissolved MeHg concentrations increased with depth indicating a net Hg methylation in deeper waters. These results are in line with several others studies in different oceanic regimes and thought to be caused by the decrease in dissolved oxygen and the remineralization of particulate organic matter (POM) that not only provides substrate for Hg methylating bacteria but also to the release from POM of reactive Hg species such as Hg chloro- or aquo-complexes that would become available for methylation (e.g. Mason and Fitzgerald, 1990; Sunderland et al., 2009, Cossa et al., 2011; Kuss et al, 2011).

A substantial increase of MeHg levels was observed at 100-200 m at station 84 where an intrusion of Upper Circumpolar Deep Water (UCDW) where there were registered low dissolved oxygen levels and an increase of dissolved iron (Puigcorbé et al., this issue). The dissolved oxygen profile presents at 100-250 m a clear bulge to lower concentrations that must be caused by strong remineralization (Figure 2). Possibly the increase of dissolved iron is caused by the stabilization of Fe(II) concentrations always associated to hypoxic conditions (Schallenberg et al., 2015). The more anoxic oceanographic conditions observed at this station and depths are more favorable for Hg methylation (Ullrich et al., 2001) therefore explaining this enhance in dissolved MeHg between 100-200m. Above and below this depth range, MeHg levels decreased suggesting less favourable conditions for methylation and/or more favourable for demethylation. At this site the absolute concentrations of Hg (and MeHg) were higher and the remineralization ratio was lower (ca. 1.72) so these results may suggest that besides methylation conditions, probably part of the Hg was not available for methylation. Moreover, Hg produced by particle remineralization could have been complexed to more refractory dissolved organic matter. The lability of organic matter in the eastern stations should not be excluded as a factor affecting activity of methylating/demethylating bacteria.

The combination on the above factors may have important repercussions in the frame of developing oxygen minimum zones (OMZ) with the consequent enhance of mercury methylation. This OMZ are particular related to climate change since model predictions and observations reveal regional declines in oceanic dissolved oxygen,

which are probably influenced by global warming (Stramma et al., 2012). Thus, these scenarios may also pose a serious environmental risk for the increase of methylated conditions in OMZ the consequent enhance of the MeHg in ocean waters.

It should be noticed that st. 140 is the only station where an almost total depletion of MeHg was observed below 80 m. It is surprising that being the same area and having the same biogeochemical and oceanographic features as station 91, the MeHg profile is very different. During the sampling of this station, the direct radiation was ten times higher (399 W m^{-2}, Table 1) than at st. 91 what could have lead to a photoreduction and demethylation. However, UV radiation (responsible for Hg photoreduction) does not penetrate more a meter in seawater (e.g. Tedetti and Sempéré, 2006) indicating that in st. 140 the MeHg depletion may not be explained by a photochemical process. Thus, in this station other factors than the ones describe above may explain the observed data. Again the bioavailability of the Hg species for methylation or even the structure of the microbial community may be important factors for the MeHg depletion in st. 140 (e.g. Ullrich et al., 2011).

At stations 143 and 174 the highest increase of MeHg with depth was found between the surface (first 60m) and bottom waters (ratio $MeHg_{bottom}/MeHg_{top}$= 34 10 at stations 143 and 174, respectively). If we assume that this enhancement is due to high remineralization of POM with the release of reactive Hg species and consequent methylation, then high remineralization rates should also be found at these stations. Thus, remineralization rates were estimated by simply calculating the ratio between POC levels in the upper 60 m (mixing layer) and at 200 m. The obtained ratios were 1.72, 2.54, 3.91 and 3.58 for stations. 84, 140, 143 and 174 respectively. At sts. 91 and 163 the ratios were not determined since the POC levels were not determined in bottom waters. Clearly there is a positive tendency for increase of MeHg and remineralization ratios. The strong positive linear correlation between the two parameters ($r=0.78$; $p<0.05$) suggests that the increase of MeHg concentrations is related to the remineralization of POC. These numbers of remineralization rates have been confirmed using the ^{234}Th levels in the study area published in this issue (Puigcorbé et al.; Roca-Martí et al.).

4.3 Relationships of mercury and methylmercury concentrations with other oceanographic parameters

Table 3 presents the correlation matrix (95% confidence level) between the concentrations of HgT and MeHg and other environmental parameters measured during this study. Positive numbers indicate positive correlations.

Significant negative correlations were obtained between both dissolved HgT and MeHg with respect to temperature ($r=-0.665$; $p<0.05$ for HgT and $r=-0.596$; $p<0.05$ for MeHg) and POC ($r=-0.603$; $p<0.05$ for HgT and $r=-0.584$; $p<0.05$ for MeHg). The negative correlation of HgT and temperature suggests that in cooler waters the amount of dissolved Hg is higher and therefore it is expected that MeHg will be also higher, if we assume that this Hg is available for methylation. Since the biotic methylation process is expected to occur in warmer waters (higher microbial activity), our results suggests that the amount of Hg available for methylation is a key factor for having more or less MeHg in this systems.

Noticeable correlations between POC and Chl-a ($r=0.610$; $p<0.05$) and between MeHg and POC ($r=-0.584$; $p<0.05$) were observed. However, no significant correlation was observed between MeHg and Chl-a ($r=-0.374$; $p>0.05$). This might indicate that organic matter of detrital origin rather than "fresh" living phytoplankton is used by Hg-methylating bacteria as a substrate.

Strong positive correlations ($r>0.72$; $n=44$) were found between Hg/MeHg with nutrients. In the eastern stations, where Hg and MeHg levels are higher, nutrient concentrations were also higher but, as stated before, it is in these stations where MeHg proportion (a proxy of the Hg methylation rate) is lower. Nutrients (including organic nutrients), are known to increase biotic Hg methylation by the stimulation of the microbial activity (Ullrich et al., 2001). However, the same supply and availability of these compounds is also known for stimulating Hg demethylation processes by aerobic bacteria which are the main demethylating agents (Pak and Bartha, 1998; Monperrus et al., 2007). The lowest Hg methylating activity (less MeHg proportion) in the eastern stations appears again to be related to the lower content of bioavailabile organic matter at these stations. In spite of the higher concentrations of Hg at station 84, the relative amount of MeHg present at this site was lower pointing out to less favourable conditions for the methylating process, possibly related to the

nature/composition of the particulate organic matter and/or increase of demethylation. In fact, this last process should not be excluded. Besides the availability of nutrient, oxygen levels were also higher at station 84 (Figure 2) suggesting that the biodegradation of MeHg can be an important process to take into account.

5. Conclusions

The present paper reports the first dataset of total mercury and MeHg concentrations in the upper 300 m in the Atlantic sector of the Southern Ocean Contrary to previous findings in other open ocean areas, it was found a high variability even in the same sector of the Southern Ocean. This fact is explained by the huge quantity of undergoing physical and biogeochemical processes such as lateral advection, upwelling of water masses or more or less favourable conditions for methylation. Overall, we found a high correlation of MeHg concentrations with respect to HgT levels.

We want to highlight the important HgT concentrations and net methylation found at station 84 south of the SPF. In this station a clear maximum of HgT and MeHg was found at 100-200 m related to the upwelling of deep low O_2 waters.

Further studies in this area should be conducted in order to confirm this subsurface methylation bulge and MeHg-HgT biogeochemistry and cycle that could have important environmental implications.

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References

Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and loss of dissolved gaseous mercury in coastal seawater, Environmental Science and Technology, 31(12): 3606–3611.

Barkay, T., Gillman, M., Turner, R.R., 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. Applied Environmental Microbiology, NOV: 4267-4271.

Bowie A. R., Lannuzel D., Remenyi T. A., Wagener T., Lam P. J., Boyd P. W., Guieu C., Townsend A. T., Trull T. W., 2009. Biogeochemical iron budgets of the Southern Ocean south of Australia: decoupling of iron and nutrient cycles in the subantarctic zone by the summertime supply. Global Biogeochemical Cycles, 23: 1–14.

Bowman, K. L., Hammerschimdt, C.R., Lamborg, C.H., Swarr, G., 2015. Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections. Deep-Sea Research II, 116: 251-261.

Bratkic, A., Vahcic, M., Kotnik, J., Vazner, K.O., Begu, E., Woodward, E.M.S., Hoervat, M., 2016. Mercury presence and speciation in the South Atlantic Ocean along the 40ºS transect. Global Biogeochemical Cycles, 30: 1–105-119.

Cheah, W., Soppa Altenburg, M., Wiegmann, S., Laglera, L.M., Santos-Echeandia, J., Strass, V., Ossebaar, S., Hoppema, M., Klass, C., Wolf-Gladrow, D., Bracher, A., n.d. Community structure and physiological state of phytoplankton across major oceanic fronts in the Southern Ocean. Deep Sea Res. Part II Top. Stud. Oceanogr. this issue.

Chaulk A., Stern G. A., Armstrong D., Barber D. G. and Wang F., 2011. Mercury distribution and transport across the ocean–sea–ice–atmosphere interface in the Arctic ocean. Environmental Science Technology, 45(5): 1865-1872.

Covelli S., Faganeli J., Horvat M., Brambati A., 1999. Pore water distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste. Estuarine Coastal Shelf Science, 48: 415-428.

Cossa, D., Heimbürger, L-H., Lannuzelb, D., Rintoul, S.R., Butler, E.C.V., Bowie, A.R., Averty, B., Watson, R.J., Remenyi, T., 2011. Mercury in the Southern Ocean. Geochimica Cosmochimica Acta, 75: 4037-4052.

EPA 2002. U. S. EPA. Method 1630: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Washington, United States, Environmental Protection Agency

Echeveste, P., Tovar-Sánchez, A., Agusti, S., 2014. Tolerance of polar phytoplankton communities to metals. Environmental Pollution, 185, 183-195.

Faucheur, S.L., Campbell, P.G.C:, Fortin, C., Slaveycova, V.I., 2014. Interactions between mercury and phytoplankton: Speciation, bioavailability, and internal handling. Environmental toxicology and Chemistry, 33(6): 1211-1224.

Fitzgerald W. F., Lamborg C. H. and Hammerschmidt C. R., 2007. Marine biogeochemical cycling of mercury. Chemical Reviews, 107: 641–662.

Gill, G.A., Fitzgerald, W.F., 1988. Vertical mercury distributions in the ocean. Geochimica Cosmochima Acta 52(6): 1719-1728.

Gill, G.A., Bloom, N.S., Cappellino, S., Driscoll, C:T., Mason, R.P., Rudd, J.W.M., 1999. Sediment-water fluxes of mercury in Lavaca Bay, Texas. Environmental Science and Technology, 33: 747-756.

Gilmour, C., Henry E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution, 71: 131-169.

Gobeil C., Macdonald R. W. and Smith J. N., 1999. Mercury profiles in sediments of the Arctic Ocean basins. Environmental Science Technology, 33: 4194–4198.

Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. Methods of seawater analysis, 3rd ed. Wiley-VCH Verlag, Weinheim, Germany.

Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H., Visscher, P.T., 2004. Biogeochemistry of methylmercury in sediments of Long Island Sound. Marine Chemistry, 90: 31-52.

Hammerschmidt, C.R., Bowman, K.L., 2012. Vertical methylmercury distribution in the subtropical North Pacific Ocean. Marine Chemistry, 132-133: 77-82.

Heimbürger L.-E., Cossa D., Marty J.-C., Migon C., Averty B., Dufour A. and Ras J., 2010. Methyl mercury distributions in relation to the presence of nano and

picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). Geochimica Cosmochimica Acta, 74: 5549–5559.

Hoppe, C.J.M., Klaas, C., Ossebaar, S., Soppa, M.A., Cheah, W., Rost, B., Laglera L.M., Santos-Echeandía J., Wolf-Gladrow, D.A., Bracher, A., Hoppema, M., Strass, V., and Trimborn, S., *in press*. Controls of primary production in two phytoplankton blooms in the Antarctic Circumpolar Current. Deep Sea Research Part II: Topical Studies in Oceanography. This issue.

Johnels, A.G., Westermark, T., 1969. Chemical Fallout, 1st Ed. Miller, Springfield, IL kiyoura 1964.

Jones, E.M., Hoppema, M., Strass, V, Hauck, J., Salt, L., Ossebaar, S., Klaas, C., van heuven, S.M.A.C., Wolf-Gladrow, D., Stöven, T., de Baar, H.J.W., 2016. Mesoscale features create hotspots of carbon uptake in the Antarctic Circumpolar Current. Deep Sea Research Part II: Topical Studies in Oceanography. This issue.

Kirk, J.L., St. Louis, V. L., Hintelmann, H., Lehnherr, I., Else, B., Poissant, L., 2008. Methylated mercury species in marine waters of the Canadian high and sub-arctic. Environmental Science and Technology, 42, 8367-8373.

Kuss, J., Zülicke, C., Pohl, C., Schneider, B., 2011. Global biogeochemical Cycles, 25: GB3021.

Laglera, L.M., Santos-Echeandía, J., Caprara, S., Monticelli, D., 2013. Quantification of iron in seawater at the low picomolar range based on optimization of bromate/ammonia/dihydroxynaphtalene system by catalytic adsorptive cathodic stripping voltammetry. Analytical Chemistry, 85(4), 2486-2492.

Lamborg, C.H., Fitzgerald, W.F:, Damman, W.H., Benoit, J.M., Balcom, P:H:, Engstrom, D.R., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. Global Biogeochemical Cycles, 16(4), 51-151-11.

Lamborg C. H., Tseng C. M., Fitzgerald W. F., Balcom P. H. and Hammerschmidt C. R., 2003. Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with “reducible Hg” titrations. Environmental Science Technology, 37: 3316–3322

Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., Swarr, G.J., Munson, K.M., Ohnemus, D.C., Lam, P.J., Heimbürger, L-R., Rijkenberg, M.J.A., Saito, M.A., 2014. A global ocean inventory of anthropogenic mercury based on water column measurements. Nature, 512, 65-69

Laurier F. J. G., Mason R. P., Gill G. A. and Whalin L., 2004. Mercury distributions in the North Pacific Ocean – 20 years observations. Marine Chemistry, 90: 3–19

Langer, C.S., Fitzgerald, W.F., Visscher, P.T., Vandal, G.M., 2001. Biogeochemical cycling of methylmercury at Barn Island salt marsch, Stonington, CT, USA. Wetlands Ecology Management, 9: 295-310.

Lehnherr, I., St. Louis, V.L., Hintelmann, H., Kirk, J.L., 2011. Methylation of inorganic mercury in polar marine waters. Nature Geoscience, 4: 298–302.

Lorrain, A., Savoye, N., Chauvaud, L., Paulet, Y. M., and Naulet, N., 2003. Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of lowcarbonated suspended particulate material. Analytica Chimica Acta, 491, 125–133.

Mason R. P. and Fitzgerald W. F., 1990. Alkylmercury species in the Equatorial Pacific. Nature, 347: 457–459.

Mason R. P. and Fitzgerald W. F., 1993. The distribution and biogeochemical cycling of mercury in the Equatorial Pacific- Ocean. Deep-Sea Research I, 40: 1897–1924.

Mason, R. P., Laurier, F.J.G., Whalin, L., Sheu, G.R., 2003, The role of ocean-atmosphere exchange in the global mercury cycle. J. Physics IV, 107: 835–838.

Mason, R. P., Morel, F.M.M., Hemond, H.F., 1995. The role of microorganisms in elemental mercury formation in natural waters. Water, Air, Soil Pollution, 80: 775–787.

Mason, R., Rolfhus, K., Fitzgerald, W., 1998. Mercury in the North Atlantic. Marine Chemistry, 61(1–2): 37–53.

Mason, R.P., Lawson, N.M., Lawrence, A.L., Leaner, J.J., Lee, J.G., Sheu, G.R., 1999. Mercury in Chesapeake Bay. Marine Chemistry, 65: 77-96.

Mason R. P. and Sullivan K. A., 1999. The distribution and speciation of mercury in the South and equatorial Atlantic. Deep-Sea Research II, 46: 937–956.

Mason R. P., Lawson N. M. and Sheu G.-R., 2001. Mercury in the Atlantic Ocean: factors controlling air–sea exchange of mercury and its distribution in the upper waters. Deep-Sea Research II, 48: 2829–2853.

Mason, R.P., Benoit, J.M., 2003. Organomercury compounds in the environment. In P. Graig Organometallic compounds in the environment, pp. 57-99. Wiley, ,West Sussex, UK.

Mason R. P. and Gill G. A., 2005. Mercury in the marine environment. In Mercury Sources, Measurements, Cycles, and Effects. Short Course, Series Volume 34 (eds. M. B. Parsons and J. B. Percival). Mineralogical Association of Canada, Halifax, Nova Scotia, Canada: pp. 179–216.

Mauro, J.B.N., Guimarães, J.R.D., Melamed, R. 1999. Mercury methylation in a tropical macrophyte: influence of abiotic parameters. Applied Organometallic Chemistry, 13: 631-636.

Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. Marine Chemistry 107: 49-63.

Moreno, F.N., Anderson, C.W.N., Stewart, R.B., Robinson, B.H. 2005. Mercury volatilization and phytoextraction from base-metal mine tailings. Environmental Pollution, 136: 341-352.

Pacyna, E.G., Pacyna, J.M., Pirrone, M., 2001. European emissions of atmospheric mercury from antrophogenic sources in 1995. Atmospheric Environment 35: 2987-2996.

Pak, K-R., Bartha, R., 1998. Mercury Methylation and Demethylation in Anoxic Lake Sediments and by Strictly Anaerobic Bacteria. Applied and Environmental Microbiology 64(3): 1013-1017.

Puigcorbé, V., Roca-Martí, M., Masqué, P., Benitez-Nelson, C.R., v. d. Loeff , M.R., Laglera, L.M., Bracher, A. Cheah, W.,Strass, V., Hoppema, M., Santos-Echeandía, J.,

Hunt, B.P.V, Pakhomov, E.A., Klaas, C. 2016. Particulate organic carbon export across the Antarctic Circumpolar Current at 10ºE: Differences north and south of the Antarctic Polar Front. Deep Sea Research Part II: Topical Studies in Oceanography This Issue.

Qureshi, A., O'Driscoll, N.J., MacLeod, M., Neuhold, Y-M., Hungerbühler, K., 2009. Photoreactions of mercury in surface ocean water: gross reaction kinetics and possible pathways. Environmental Science and Technology 44(2): 644-649.

Roca-Martí, M., Puigcorbé, V., Iversen, M.H., van der Loeff, M.R., Klaas, C., Cheah, W., Bracher, A., Masqué, P. 2016. High particulate organic carbon export during the decline of a vast diatom bloom in the Atlantic sector of the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography This Issue.

Rolfhus, K. R., Fitzgerald, W.F., 2001. The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY. Geochimica Cosmochimica Acta, 65(3): 407–418.

Schallenberg, C., Davidson, A.B., Simpson, K.G., Miller, L.A., Cullen, J.T., 2015. Iron(II) variability in the northeast subarctic Pacific Ocean. Mar. Chem. 177, Part 1, 33-44.

Stramma, L., Prince, E.D., Schmidtko, S., Luo, J., Hoolihan, J.P., Visbeck M., Wallace, D.W.R., Brandt, P., Körtzinger, !., 2012. Expansion of oxygen minimum zones may reduce available habitat for tropical pelagic fishes. Nature Climate Change 2: 33–37

Strass, V. H., H. Leach, H. Prandke, M. Donnelly, A. U. Bracher and D. A.Wolf-Gladrow, 2016. The physical environmental conditions of biogeochemical differences along the ACC in the Atlantic Sector during late austral summer 2012. This Issue.

Strode, S., Jaegle, L., Selin, N., Jacob, D., Park, R., Yantosca, R., Mason, R., Slemr, F., 2007, Air-sea exchange in the global mercury cycle. Global Biogeochemical Cycles, 21, GB1017.

Sunderland E. M., Krabbenhoft D. P., Moreau J. W., Strode S. A. and Landing W. M., 2009. Mercury sources, distribution, and bioavailability in the North Pacific Ocean: insights from data and models. Global Biogeochemical Cycles 23, 1-15.

Tedetti, M., Sempéré, R., 2006. Penetration of ultraviolet radiation in the marine environment. A review. Photochemistry and Photobiology, 82(2): 389-397.

Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in aquatic environment: a review of factors affecting methylation. Critical Reviews in Environmental Science and Technology, 31(3): 241-293.

Zhang, Y., Jaeglé. L., Thompson, L., 2014. Natural biogeochemical cycle of mercury in a global three-dimensional ocean tracer-model. Global Biogeochemical Cycles, 28, 553-570.

Zhong, H., Wang, W-X., 2009. Controls of dissolved organic Matter and chloride on mercury uptake by a marine diatom. Environmental Science and Technology, 43(23): 8998-9003.

Figure and Table Captions

Figure 1. Study area with the sampling stations.

Figure 2. Vertical profiles of salinity (psu), temperature (ºC) and dissolved oxygen (µmol kg^{-1}) at each sampling station.

Figure 3. Vertical profiles of nitrite, nitrate, phosphate and silicate concentrations (µmol L^{-1}) at each sampling station.

Figure 4. Vertical profiles of *chlorophyll a* (µg L^{-1}) at each sampling station.

Figure 5. Vertical profiles of particulate organic carbon (POC, µg L^{-1}) and dissolved organic carbon (DOC, µg L^{-1}) at each sampling station.

Figure 6. Vertical profiles of total dissolved Hg and MeHg (ng L^{-1}) in the six sampling stations. Note the difference in the y-axis scale for station 84 (500 m instead of 300 m depth). Values below detection limit have been ploted with the values of the detection limit (0.1 ng L^{-1} for HgT and 0.02 ng L^{-1} for MeHg) and are shown with a grey dot (dark for HgT and light for MeHg).

Figure 7. Relationship between HgT and MeHg concentrations (ng L^{-1}) obtained for all samples (samples with MeHg below detection limit (DL) were excluded). White dots correspond to station 84 (unfiltered water).

Table 1. Total dissolved Hg and MeHg concentrations (ng L^{-1}) at all stations sampled during the Eddy Pump cruise, depth range 0-300 m.

Table 2. Concentrations of HgT and MeHg (ng L^{-1}) obtained in this study and in other similar studies for the Atlantic and Southern Ocean waters.

Table 3. Correlation matrix between Hg, MeHg and ancillary parameters measured at all the stations and depths. Positive numbers indicate positive correlations. Figures in bold when the correlation is statistically significative ($p<0.05$).

Figure 1

Figure 1

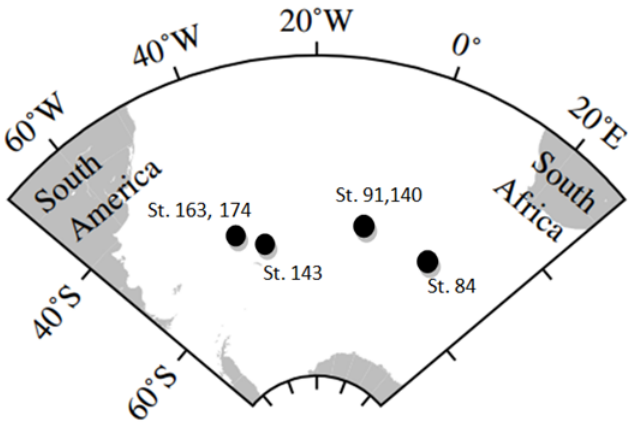


Figure 2

Figure 2

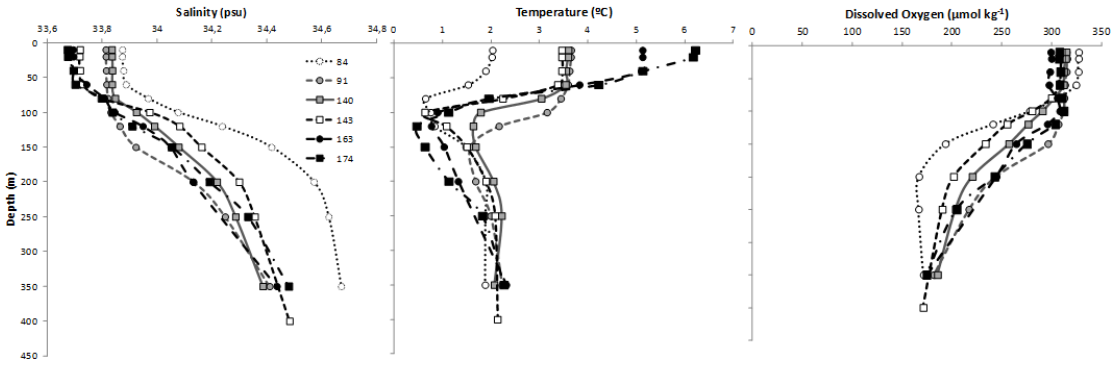


Figure 3

Figure 3

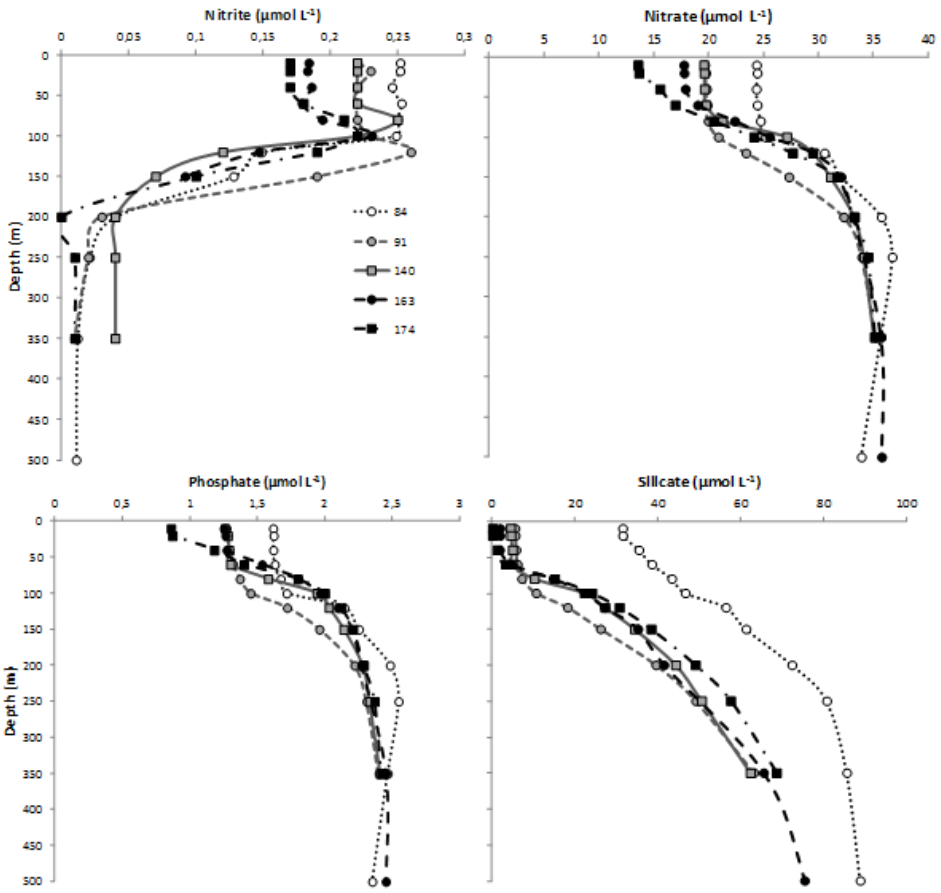


Figure 4

Figure 4

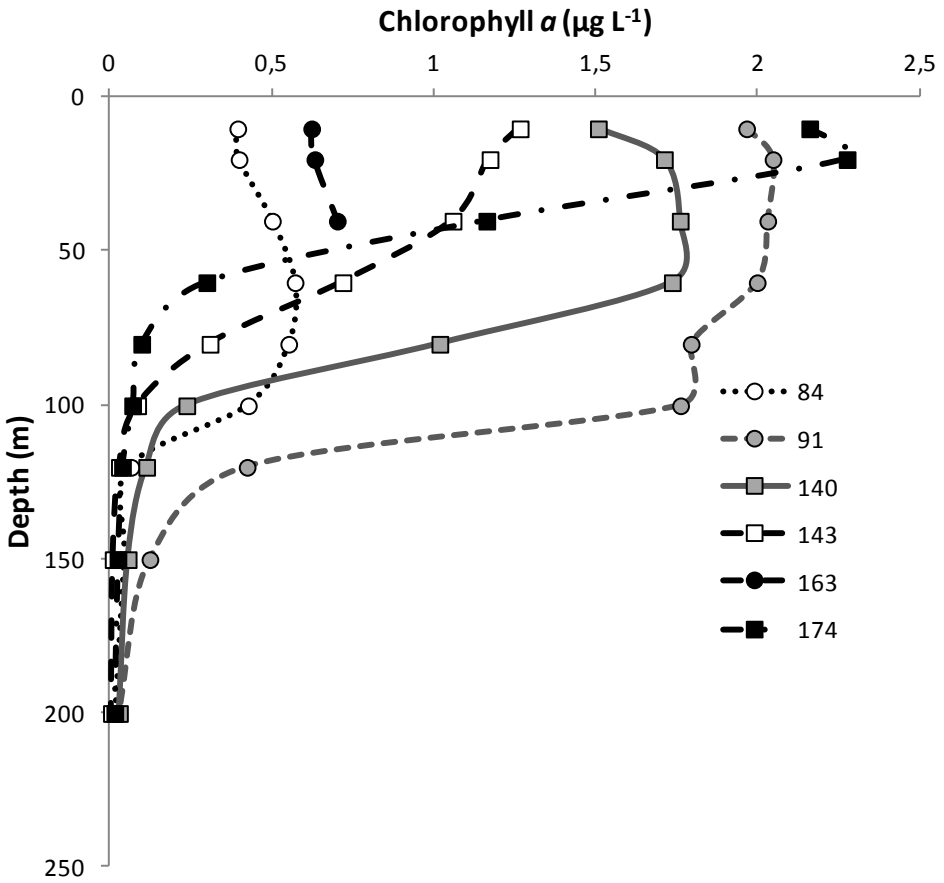


Figure 5

Figure 5

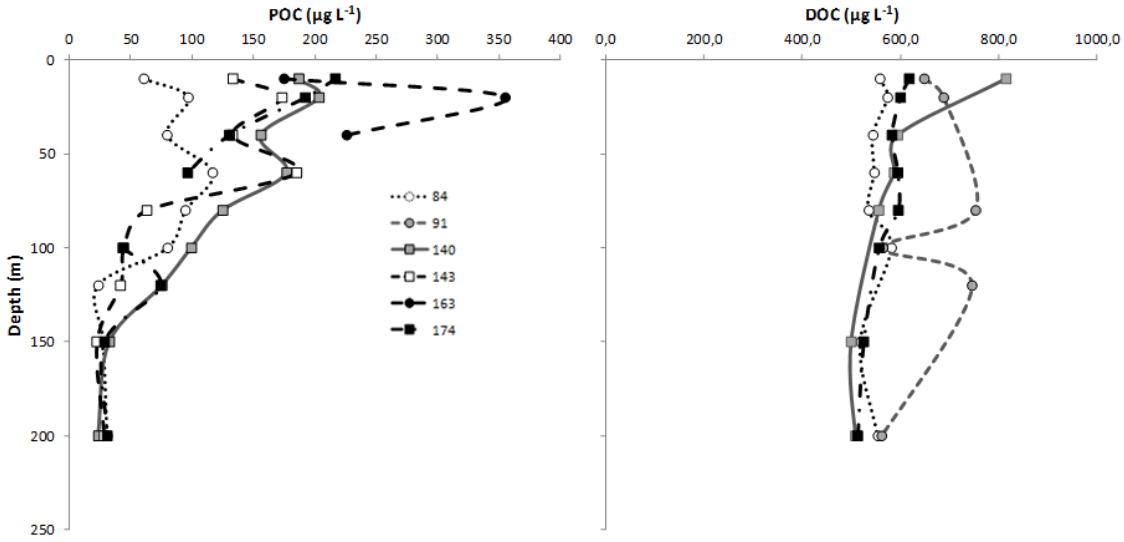


Figure 6

Figure 6

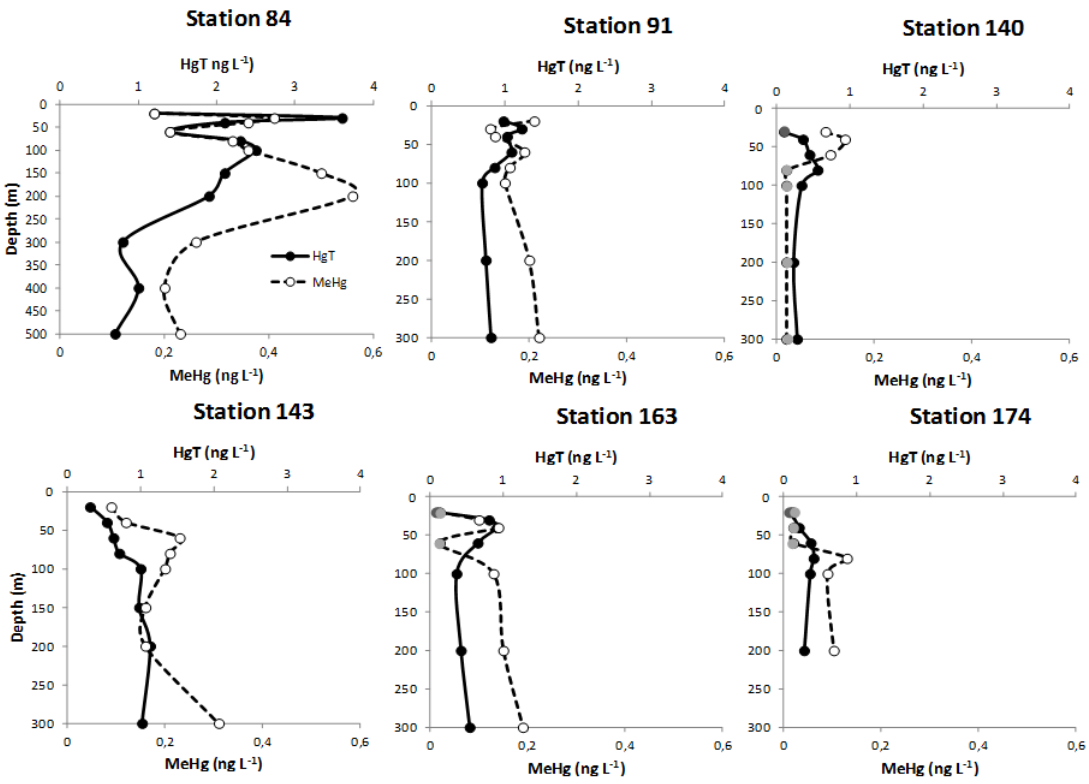
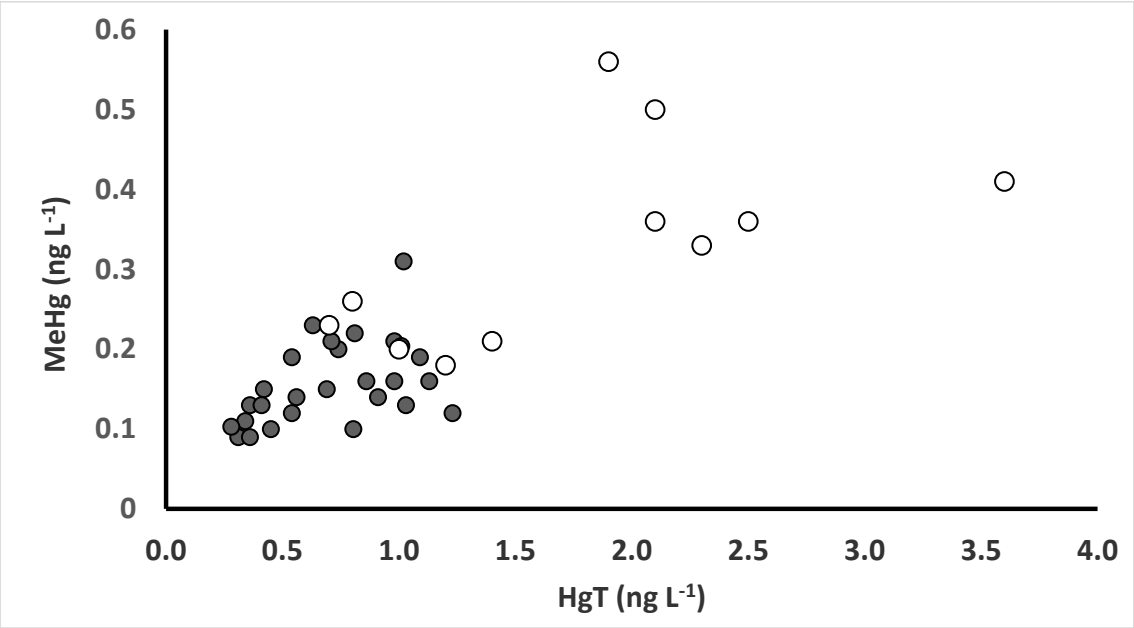


Figure 7



Table

Table 1

Station	Date	Lat	Long	ML depth (m)	Direct Radiation (W m^{-2})	HgT (ng L^{-1})	MeHg (ng L^{-1})	MeHg (%)	Features
84*	21.01.2012	-53.00	10.01	55	0	0.70 - 3.60	0.18 - 0.56	11 - 33	South of the SPF**
91	03.02.2012	-51.20	-12.67	56	34±28	0.69 - 1.23	0.12 - 0.22	10 - 27	Phytoplankton bloom:
140	17.02.2012	-51.20	-12.66	68	399±117	0.23 - 0.56	0.10 - 0.14	22 - 32	medium-final stage
143	24.02.2012	-53.5	-36.40	59	0	0.31 - 1.13	0.09 - 0.31	14 - 37	Island effect
163	28.02.2012	-50.40	-39.40	39	0	0.36 - 0.91	0.10 - 0.19	12 - 36	Bloom decay
174	01.03.2012	-49.65	-38.29	39	795±28	0.21 - 0.54	0.09 - 0.19	25 - 37	Phytoplankton bloom

*Unfiltered water **SPF: Sub Polar Front

Table 2

Sites	HgT (ng L^{-1})	MeHg (ng L^{-1})	Reference
Southern Ocean (East Antarctica)	0.13 - 0.55	0.04 - 0.19	Cossa et al., 2011
South Atlantic (Antarctic Bottom Waters)	0.13 - 0.19	-	
South Atlantic (Thermocline)	0.08 - 0.13	-	Lamborg et al., 2014
Southern Ocean (Thermocline)	0.19 ± 0.01	-	
North Atlantic	0.19 - 0.22	-	
Canadian Arctic Archipelago	0.40 ± 0.47	0.024 - 0.178	Kirk et al., 2008
North Atlantic	0.18 ± 0,06	0.02 ±0.02	Bowman et al., 2015
North Pacific Ocean	≈ 0.06 - 0.30	≈ DL - 0.02	Hammerschmidt et al., 2012
South Atlantic Ocean	0.29 ±0.12	≈ DL – 0.05	Bratkic et al., 2016
Southern Ocean	DL – 1.22	DL – 0.31	Present study
Southern Ocean (st. 84)*	0.70 – 3.58	0.18 – 0.56	

Note: Some of the presented levels were converted from the original concentration (molar units) to ng L^{-1} for better comparison

Table 3

	HgT	MeHg	S	T	O2	Nitrite	Nitrate	Phosphate	Silicate	Chl a	DOC	POC
HgT	1											
MeHg	**0,821**	1										
S	**0,593**	**0,543**	1									
T	**-0,665**	**-0,596**	**-0,847**	1								
O2	**0,626**	**0,611**	**0,865**	**-0,836**	1							
Nitrite	**0,718**	**0,538**	**0,971**	**-0,977**	**0,877**	1						
Nitrate	**0,783**	**0,621**	**0,897**	**-0,977**	**0,804**	**0,954**	1					
Phosphate	**0,766**	**0,62**	**0,794**	**-0,926**	**0,703**	**0,863**	**0,971**	1				
Silicate	**0,785**	**0,648**	**0,708**	**-0,852**	**0,842**	**0,797**	**0,868**	**0,85**	1			
Chl a	-0,361	-0,374	-0,102	0,434	-0,166	-0,303	**-0,559**	**-0,701**	**-0,636**	1		
DOC	-0,119	-0,251	-0,074	0,227	-0,361	-0,135	-0,242	-0,298	**-0,520**	**0,512**	1	
POC	**-0,603**	**-0,584**	**-0,554**	**0,666**	**-0,756**	**-0,648**	**-0,613**	**-0,578**	**-0,711**	**0,610**	**0,541**	1